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1911

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THE INFLUENCE OF ORGANIC LIQUIDS UPON THE INTERACTION OF HYDROGEN SULPHIDE AND SULPHUR DIOXIDE

BY DAVID KLEIN

SOCIÉTÉ CHIMIQUE DE FRANCE
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Introduction

Numerous examples of the influence of slight amounts of water upon chemical changes of various kinds are on record. But similar studies of the effect of liquids other than water are few and fragmentary. So it has seemed that a systematic investigation of the influence of organic liquids upon a gaseous system, incapable of decomposition in the dry state, would be of considerable value in gaining an understanding of the mechanism of chemical change, as well as in formulating a theory of solutions.

Because of its abundance, and its great solvent power (for some classes of substances), water is regarded by certain chemists as having exceptional properties. "Water is a substance whose presence in at least minute amounts seems to be essential to the occurrence of most chemical reactions. Moreover, its method of action is probably unique, consisting either in a hydration or electrolytic dissociation of the reacting substances. It is therefore not inappropriate that it alone constitutes a type of catalytic agent."[1] However, the results of the present investigation clearly show, at least as far as one property of water is concerned, namely its ability to accelerate chemical changes, that other liquids have that characteristic in a no less marked degree.

The action between hydrogen sulphide and sulphur dioxide was selected as suitable for an experimental investigation. It is difficult to state who first studied this reaction; certainly, it was known a century and a quarter ago. In 1812 Cluzel[2] discovered that the gaseous system would not be decomposed unless moisture is present. The gases after being

[1] Noyes and Sammet: Jour. Am. Chem. Soc., 24, 498 (1902).
[2] Cluzel: Ann. Chim. Phys., 84, 162 (1812).

dried by fused calcium chloride were mixed in varying proportions in a glass container over mercury. Depending upon the degree of desiccation, the period of no action varied from fifteen minutes to five hours. Experiments conducted in the absence of sunlight, showed no difference in action, when compared with similar tests, performed in sunlight. Cluzel summarizes his work as follows: "*Que l'hydrogène sulfuré et l'acide sulfureux peuvent rester assez longtemps en contact sans se décomposer, quand ils sont bien secs et qu'il est très-probable qu'ils ne se décomposeraient pas si on les faisait arriver très-secs dans un appareil où il ny eût aucun corps qui exerçât une affinité sur le soufre.*"

Then, in 1868, Schmidt[1] published a note on the influence of moisture on the gaseous mixture: "*Nachdem ich die Angabe Vogel's (Gmelin. Handb. 643), dass gewöhnliche Schwefelsaüre von Schwefelwasserstoff zersetzt wird, bestätigt, beobachtete ich die Bildung von schwefliger Saüre bei Übergiessen fein gepulverter oder gefällter Schwefelmetalle mit concentrirter Schwefelsaüre, so zwar, dass rauchende keinen oder nur ein Minimum von Schwefelwasserstoff auftreten lässt. Die fraglichen beiden Agentien vollkommen trocken gemischt, reagiren nicht auf einander; führt man in das Gefäss einen benetzten Glasstab, so zeichnen sich die berührten Stellen momentan durch ausgeschiedenen Schwefel und die Pentathionsaüre tritt auf.*"

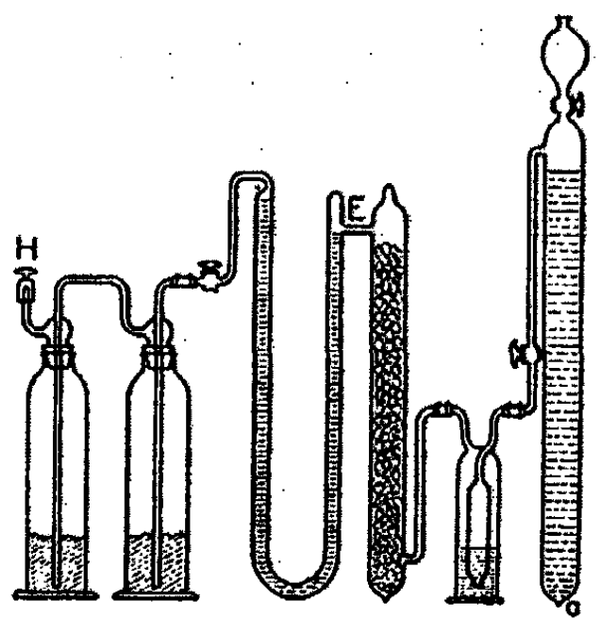
Apparatus and Method

The experimental parts of this investigation may be conveniently divided among several general heads; (1) the preparation, drying and storing of the pure gases, (2) the devising of a suitable reaction vessel, (3) the preparation of pure dry organic liquids.

Hydrogen sulphide.—After many unsatisfactory trials

[1] W. Schmidt: Zeit. für Chemie (Beilstein-Fittig), 11, 50 (1868). The University of Wisconsin does not possess this periodical; but a copy was kindly loaned by the Mass. Inst. of Technology, for which I herewith wish to express my gratitude. Since the article in question is not readily accessible, it was thought worth while to reprint it in full.

with various substances for the preparation of pure hydrogen sulphide, such as calcium sulphide and antimony sulphide, it was found that the action of hydrochloric acid upon zinc sulphide would yield a very pure gas in quantities that were readily controlled. The means for drying and storing the gas are represented in Fig. 1. The generator A was constructed out of a dropping funnel and a Liebig condenser jacket. It was filled in the inverted position through *a*, which was then sealed off. B is an ordinary wash bottle, containing pure water, to free the gas from any hydrochloric acid vapors. C, a large calcium chloride tower, was constructed from a



G F D C B A

Fig. 1

Liebig condenser jacket. D is a large U-tube, made by bending a glass tube 4′ long and $^5/_8$″ in diameter. After being filled with phosphorus pentoxide, it was sealed to C at E. The dried gas was stored in two 500 cc Drechsel wash bottles (F * G) containing some phosphorus pentoxide. Some connections were made by sealing the tubes together, while others consisted of heavy rubber tubing. The latter gave no trouble, but, if necessary, could be eliminated.

The train was first exhausted by means of a water pump; then filled with the gas, by allowing concentrated hydrochloric acid to flow down from the dropping funnel. The

exhaustion and refilling were repeated until the issuing gas was completely absorbed by a caustic potash solution.

Sulphur dioxide.—For the preparation of this gas concentrated hydrochloric acid was allowed to act on pure sodium acid sulphite, contained in the generator A (Fig. 2). Addi-

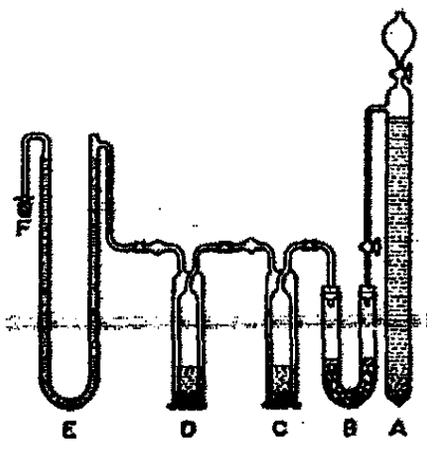


Fig. 2

tional parts of the train were a wash bottle B containing pure water, to remove hydrochloric acid; two Wetzel bottles (C–D) capacity 500 cc; containing conc. sulphuric acid; a large U-tube E made by bending a glass tube 3′ × $^{5}/_{8}$″, and filled with phosphorus pentoxide. It might be well to state at this point that all the phosphorus pentoxide used in these experiments was the ordinary variety, supplied either by Merck or Schuchardt.

Reaction vessel.—This was made out of a condenser jacket (300 cc) and stop-cocks (the ordinary two-way variety). (A. Fig. 3). Branch *c* was connected with the sulphur

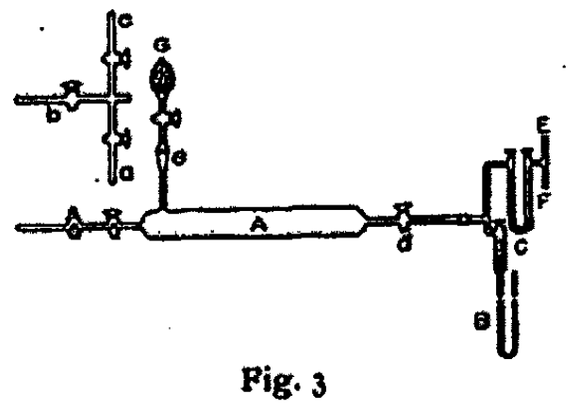


Fig. 3

dioxide generator; branch *a* likewise with the hydrogen sulphide train. Through *b* a current of air, dried by sul-

phuric acid and phosphorus pentoxide, was slowly aspirated by means of a water pump. The exit tube *d* was protected from the moisture of the pump E by a six-inch Schwartz tube, containing phosphorus pentoxide. A second similar guard bulb was attached to the Sprengel pump F; while a third one was connected with the open manometer B. At *e* is a ground glass joint, accurately fitted to the vessel G, which served as the receptacle for the pure organic liquid. The bulb was an ordinary 25 cc acetylization flask, to which was sealed a stop-cock. Connection of the reaction chamber to the various parts of the apparatus was made with thick-walled rubber tubing, the ends of the glass tubing being pushed as close together as possible.

The purification of the organic liquids was carried out as follows: In the first place, the purest sample of the particular liquid that the laboratory afforded, was subjected to ordinary fractional distillation. The desired portion was collected in an eight-ounce bottle (commonly known as a specimen bottle) provided with an accurately ground stopper. Previous to use, these bottles were thoroughly cleaned, rinsed with very pure distilled water, and dried in an air bath at 160° C for 3–5 hours. They were kept in a desiccator containing phosphorus pentoxide. The appropriate drying agent was added to the liquid, with which it remained in contact, with frequent shaking, for varying periods of time.

After each experiment the reaction vessel was coated with a film of sulphur. For the rapid and complete removal of this layer, fuming nitric acid was found very efficient. After being thoroughly rinsed with distilled water, the apparatus was steamed out, the steam being evolved from water to which sulphuric acid and potassium bichromate were added. Steam is a very delicate test for grease, since the latter supplies nuclei for the condensation of water vapor, thus causing drops to form on any unclean portion of the vessel. All visible moisture was removed by aspirating warm air through the apparatus. The stop-cocks and bores were

carefully wiped with a clean, fat-free cloth, after which they were thinly coated with a rubber composition lubricant.

The lubricant is the one recommended by Travers.[1] It was used in all experiments, excepting a few trials with phosphoric acid, made by exposing phosphorus pentoxide to the air. However, it was found that this substance would cause the gases to react, and was therefore discarded.

When the reaction vessel was cleaned, dried and set in position, the catalytic liquid was subjected to a final distillation. This was accomplished in the special apparatus, shown in Fig. 4. It consisted of a 150 cc distilling flask A to which

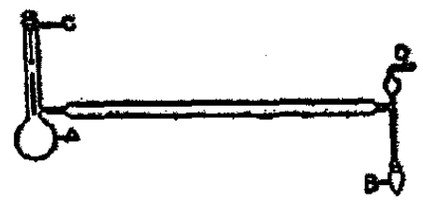


Fig. 4

was sealed a limb of a Schwartz tube. A condenser was also sealed to the flask. As a receiver B a 25 cc acetylization flask was used, so chosen that its ground joint would fit very closely the small flask to be attached to the reaction chamber. To suspend a thermometer in the flask, a piece of fusible glass was bent so that the head could be inserted in the glass stopper, if held at an angle, but was too large to slip out if held vertically. From this hook a suitable thermometer was suspended by a platinum wire.

The distilling apparatus was thoroughly dried by drawing through it a current of air, that had passed through conc. sulphuric acid and phosphorus pentoxide. Tubes of the latter material also prevented the access of any moisture from the pump D. After the air had thus passed for several hours at ordinary temperatures, the apparatus was highly heated with a free Bunsen flame. Dry air was continually aspirated through C, until room temperature was again restored. Then the stopper was quickly removed, the liquid poured in, and

[1] "Study of Gases."

distilled. After the condenser had been thoroughly moistened with the distilled liquid, the receiver was quickly replaced by the bulb which up to this time was kept in a desiccator over phosphorus pentoxide. When filled with the liquid, the bulb was very quickly detached and fitted with its own stopper, which was described before.

The bulb was attached to the reaction vessel. A current of dry air at room temperature, was drawn through the apparatus for hours (varying from 6 to 20), after which the drying was continued, while the apparatus was being highly heated with a free Bunsen flame. This last operation was continued for an hour. Then the reaction vessel was evacuated as far as possible by means of a water pump. To reduce the pressure as completely as possible, the final exhaustion was effected with a good Sprengel pump. The pressure was noted on a closed manometer on the pump and also on an open manometer (B Fig. 3). To fill the vessel with the reacting gases in the proper proportion, sulphur dioxide was allowed to slowly enter until the pressure had risen to one-third the atmospheric pressure as read on the open manometer. The hydrogen sulphide was admitted, to make up the other two-thirds. All stop-cocks were closed, so that the mixture was contained in an apparatus entirely of glass, except for the lubricant on the stop-cocks.

The mixture was allowed to remain an hour or more, to be sure that no action occurred spontaneously. Then by opening the stop-cocks to the catalyzer bulb (G Fig. 3) and gently warming the latter, enough liquid (never more than a few cc) could be admitted into the reaction chamber. The detailed observations will be given below.

Results.—Since the procedure in nearly all cases was essentially that given above, it is not necessary to repeat it in discussing the various liquids.

Benzol.—Some of Kahlbaum's recrystallized thiophene-free product was dried with phosphorus pentoxide for four months. In the first trial there was no action in three hours. A few drops of water were poured into the reaction vessel by

quickly raising and replacing the catalyzer bulb. There was immediate action. Subsequently on opening tap *d* (Fig. 3) under water, the liquid completely filled the vessel. In fact, this check upon the purity of the mixture was performed after each experiment.

The experiment was repeated with a new, freshly distilled sample of benzol, with the result that there was no action within an hour and thirty minutes.[1]

Carbon tetrachloride.—The liquid was dried with phosphorus pentoxide for two weeks. Not the slightest sign of action within an hour. Repeated experiment, with a freshly distilled sample of the same liquid, with similar results.

Chloroform.—This was dried for three days with phosphorus pentoxide. It produced no action within an hour. A second trial gave the same result.

Ethyl alcohol.—Ordinary alcohol was treated with calcium carbide, by boiling under a reflux condenser. The acetylene was removed by distilling under diminished pressure, and then by treating with bromine. The product was twice fractionated after adding sodium. As soon as the first drop of this liquid entered the reaction vessel, there was intense action.

A repetition of the experiment with a sample of this alcohol, after a third distillation with sodium, gave a similar result. After this experiment a very slight odor of acetylene was noticeable in the alcohol, so that the results were not conclusive, although, as will appear later, the action must be attributed to the alcohol.

A new sample was prepared as follows: Ordinary alcohol was boiled under a reflux condenser with pure lime for six hours; then distilled. It was similarly treated with barium oxide.[2] A final distillation was made after treatment with

[1] It must not be inferred that action occurred after this period. Here and elsewhere in this paper, where a similar expression occurs, it means that the experiment was discontinued at this point.

[2] I have found barium oxide a most efficient drying agent. The easiest way to prepare a suitable product was to heat anhydrous barium peroxide to

sodium. As in the two previous trials, the first drop caused instantaneous action.

Amylene.—A Schuchardt preparation was dried for three days over fused calcium chloride. The portion boiling between 40°–41° was employed. There was no visible action in over an hour. A drop of water caused an immediate deposition of sulphur.

Acetone.—Merck's C. P. product was dried for four days with anhydrous sodium sulphate, before redistilling. Immediate action occurred as soon as the first drop entered the apparatus.

Repeated with a portion of the acetone that had remained in contact with the drying agent for two days longer. Similar results were obtained as in the preceding trial.

A third experiment was performed with a sample of Kahlbaum's acetone, that had been standing over fused calcium chloride for seven weeks. As in the other trials, the reaction began immediately.

Ether.—The material was obtained from Professor Koelker, who had rendered it absolute from the commercial variety by treatment with calcium chloride and then with sodium. It was further dried over sodium and distilled from a fresh portion of that metal. The reaction was rather slow at first, but in less than two minutes it proceeded rapidly, due in part at least, to autocatalysis.

The experiment was repeated after continued treatment with sodium, with similar results, as in the first trial.

Methyl cyanide.—Merck's product was redistilled after being dried with fused calcium chloride for five days. After treatment with phosphorus pentoxide for four days, it was again distilled. Throughout the manipulations, the liquid boiled very constantly. For thirty-five minutes, the liquid caused no action. Then the reaction vessel became coated with a light yellow deposit.

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redness for an hour and then cool the product in a desiccator over phosphorus pentoxide. The mass was quickly pulverized and sealed in small portions in test tubes.

Ethyl disulphide.—The sample was a Schuchardt preparation. It was a yellow, oily liquid with a very disagreeable odor. No attempt was made at purification. The liquid was simply poured into the dried catalyzer bulb. Even after an hour's contact, there was not the slightest sign of action. A few drops of water produced immediate reaction. After several hours a large portion of the sulphur had dissolved in the ethyl disulphide.

Carbon bisulphide.—Ordinary carbon bisulphide was purified by shaking for hours with mercury; then decanting and shaking with potassium permanganate. It was again decanted, and after further treatment with mercury, it was redistilled. In twenty-five minutes there was no visible change. Then the glass in the T tube around the stop-cocks became coated with sulphur, although the liquid remained perfectly colorless and transparent. Of course, the action finally continued to completion.

The above experiment was repeated, after the carbon bisulphide had been further shaken with mercury. The same phenomena were noted as in the previous trial. During the first twenty-one minutes there was no action; then a distinct clouding of the T tube occurred, but the liquid remained clear.

A third trial with some carbon bisulphide that had been in contact with mercury for six months, gave no action in an hour and ten minutes. After that, the same clouding of the T tube was observed, while the liquid remained clear.

From these experiments it was evident that the lubricant was a disturbing factor. To eliminate this source of trouble, a reaction chamber was constructed, similar to the one used in all other cases with the exception that no stop-cocks were used. Instead the tubes were constricted in order to seal them off.

The catalyzer was contained in a little glass bulb, which was placed in the apparatus before sealing on the T tube. The obtaining of the liquid was necessarily different from the usual method. A receiver was devised, consisting of a large

bulb and a small glass tube, each sealed to a branch of a T tube. The third branch was sealed to a large adapter, which fitted over a two-hole stopper, to accommodate the condenser tube and a guard tube of phosphorus pentoxide. The condenser was pushed down into the adapter as far as possible, to avoid contact of the carbon bisulphide fumes with the rubber stopper. The receiver was packed in an ice-salt mixture. The idea of the peculiarly shaped receiver was that the distillate could first be collected in the large bulb, but when the desired fraction was obtained, it could be diverted into the small tube by slightly turning the receiver. When enough of the liquid was obtained, the small tube was sealed off.

As to the drying and filling of the apparatus, the manipulation was the same as in the other cases. After admitting the sulphur dioxide, the tube connecting the reaction vessel with the sulphur dioxide train was sealed off. In like manner the other tubes were sealed. A very slight deposition of sulphur occurred when the tube leading to the hydrogen sulphide train was sealed; but there was no visible increase in this deposit in forty-five minutes, probably because of slowness of diffusion in so small a tube.

The bulb containing the carbon bisulphide was broken by shaking the apparatus. There was no visible action in an hour and five minutes. Upon the supposition that the carbon bisulphide might have dissolved the sulphur as fast as it formed, the end of the apparatus was broken under mercury. There was no appreciable rise. Upon the admission of a few drops of water, immediate action ensued.

Ethyl chloride.—The material was the usual liquid employed for anaesthesia. It was contained in a sealed glass tube, which was broken and the contents were rapidly poured into the catalyzer container. A large portion of the liquid vaporized, but enough was secured for a fair trial. After forty-five minutes of contact, the liquid seemed not at all affected. A little more of it was forced into the reaction vessel, whereupon the pressure became so great as to violently force out the ground joint and break it.

Benzoyl chloride.—A fresh unopened bottle of Kahlbaum's make was used as the catalyzer, without any special purification. The liquid was simply poured into the dried catalyzer container. There was no action in forty-five minutes. Water caused an immediate deposition of sulphur.

The experiment was repeated with the same liquid. There was no action in three and one-half hours.

Methyl benzoate.—A Schuchardt preparation was dried over fused calcium chloride for four days and then distilled under diminished pressure. For the first twenty-five minutes there was no action; then sulphur was rapidly deposited.

Acetyl chloride.—An unopened bottle of Merck's product was used without any attempt at purification. There was no reaction in two hours and twenty minutes. Water caused an immediate precipitation of sulphur.

Benzaldehyde.—A Schuchardt preparation was dried for four days over fused calcium chloride, after which it was distilled in a current of carbon dioxide under diminished pressure. Immediately after the admission of the catalyzer it assumed a greenish color, then a yellow one, and in a few minutes, sulphur was deposited.

Carvone.—This compound is of special interest, since it forms a definite crystalline compound with hydrogen sulphide. The material was labelled "Chemically Pure Carvol" Schimmel & Company. The liquid was dried over anhydrous copper sulphate for three days. The portion boiling between 222°–224° was used. It had a very slight yellow tinge. There was instantaneous action as soon as the liquid entered the reaction chamber.

Benzyl cyanide.—A Schuchardt specimen was dried over anhydrous copper sulphate for four days. In less than two minutes, after it was admitted into the reaction vessel, there was formed a distinct yellow deposit.

Propyl acetate.—A Schuchardt sample had been standing for years over fused calcium chloride. Reaction ensued as soon as the liquid entered the reaction vessel.

Amyl alcohol.—A redistilled Kahlbaum preparation was

dried over calcium chloride for two days and over anhydrous copper sulphate for six days. It boiled very constantly. There was instantaneous action when the liquid entered the catalyzer vessel.

The experiment was repeated with a different sample of Kahlbaum's make, that was refractionated and then dried over barium oxide for eight days. The barium oxide showed extremely little hydration, a state that was easy to detect, inasmuch as the anhydrous oxide was gray, while the hydrate was a pure white. As in the preceding trial, there was an instantaneous deposition of sulphur. The next morning many monoclinic sulphur crystals were noted in the amyl alcohol. This phenomenon is not anomalous, as other cases are on record of sulphur crystallizing in the monoclinic system at ordinary temperatures.

Propionitrile.—A good sample was dried for eight days over barium oxide The drying material seemed unaffected. For the first seven minutes, after introducing the liquid, there was no visible action. Then the liquid became cloudy.

Isobutyl alcohol.—A redistilled Kahlbaum product was dried for five days over barium oxide. It distilled quite constantly. The liquid caused immediate, vigorous action. The experiment was repeated, using the above sample of the alcohol after it had remained over barium oxide for three days longer, and had then been treated with sodium. The boiling point was unchanged. Reaction proceeded exactly as in the previous trial.

Isobutyl acetate.—A redistilled Schuchardt preparation was dried over barium oxide for two weeks. For the first six minutes, after entering the reaction vessel the liquid remained transparent, then it became clouded, and soon a dense deposit of sulphur was formed.

Nitrobenzene.—A Schuchardt product was redistilled. It caused no action in an hour and forty-five minutes. Water produced an instantaneous precipitation.

Valeronitrile.—A good sample was refractionated; then dried for ten days over anhydrous copper sulphate and for two

days over barium oxide. For the first fifteen minutes after admitting the liquid, there was no action. Then the liquid became cloudy.

Methyl ethyl ketone.—A previously unopened bottle of Schuchardt's make was dried for two days over barium oxide. In less than two minutes after entering the reaction vessel, the liquid clouded.

TABLE 1

		Action	Dielectric constant	Association factor
Water	H_2O	immediate	80.0	3.60
Ethyl alcohol	C_2H_5OH	"	25.8	2.74
Isobutyl alcohol	C_3H_7OH	"	20.0	1.95
Isoamyl alcohol	$C_5H_{11}OH$	"	16.0	1.97
Acetone	CH_3COCH_3	"	25.0	1.26
Methyl ethyl ketone	$CH_3COC_2H_5$	less than two min.	17.8	1.15
Acetonitrile	CH_3CN	after 15 min.	36.4	1.60
Propionitrile	C_2H_5CN	after 7 min.	26.5	1.77
Valeronitrile	C_4H_9CN	after 15 min.	17.4	—
Benzyl cyanide	$C_6H_5CH_2CN$	after 2 min.	14.9	—
Methyl benzoate	$C_6H_5COOCH_3$	after 25 min.	6.58	—
Propyl acetate	$CH_3COOC_3H_7$	immediate	5.73	—
Isobutyl acetate	$CH_3COOC_4H_9$	after 6 min.	5.26	—
Ether	$(C_2H_5)_2O$	less than two min.	4.3	1.04
Benzaldehyde	C_6H_5CHO	immediate	17.7	0.97
Carvone	$C_{10}H_{14}O$	"	—	—
Carbon bisulphide	CS_2	none	2.64	1.67
Ethyl disulphide	$(C_2H_5)_2S_2$	"	7.2	—
Benzol	C_6H_6	"	2.28	1.01
Amylene	C_5H_{10}	"	2.20	0.96
Chloroform	$CHCl_3$	"	5.14	0.94
Nitrobenzene	$C_6H_5NO_2$	"	36.45	0.93
Acetyl chloride	CH_3COCl	"	25.30	1.06
Benzoyl chloride	C_6H_5COCl	"	—	—
Ethyl chloride	C_2H_5Cl	"	6.29	—
Carbon tetrachloride	CCl_4	"	2.25	1.01

Discussion

The experiments have been reported in considerable detail, because the experience of the author with the work of other investigators along similar lines seemed to warrant it. Thus, the report of the classic work of Baker on ammonia

and hydrochloric acid contains so little of the necessary manipulating directions that a repetition of his experiment is an extremely difficult matter.

Experimentation of the kind involved in this paper is always open to the general objection that the substances which induce action may not have been sufficiently dry or pure. Of course, this criticism is unanswerable. On the other hand, to maintain that the reacting substances were "absolutely dry," a phrase one frequently meets in the writings of reputable chemists, would require proof that could not be furnished. The best that can be done is to give an accurate and detailed description of the apparatus and method, so that others may be able to repeat the work.

The selection of methods employed in this investigation might be questioned by some who have had experience with reactions in moisture free media. For instance, the failure to use redistilled phosphorus pentoxide would seem to invalidate the results and conclusions. But arguments of this nature lose much of their force, when the fact is taken into consideration that both positive and negative results were obtained under working conditions that were as similar as it was possible to make them.

But another reason for confidence in the method lies in the fact that Baker has obtained similar results for ethyl alcohol and carbon tetrachloride. While no statement of his experimental methods has appeared, his results form the concluding paragraph of the Wilde lecture for 1909.[1]

"Mr. J. C. Thomson has recently done some experiments for me on the hydrogen sulphide and sulphur dioxide mixture. He finds that liquid alcohol and liquid sulphur dioxide (both having high specific inductive capacity) can bring about the decomposition in the mixture, while carbon tetrachloride, whose specific inductive capacity is low, is inert. Also, metallic aluminum and metallic mercury are apparently unable to affect the change."

While the dependence of chemical activity upon specific

[1] Mem. and Proc. Manchester Lit. and Phil. Soc., Vol. 53, Part III.

inductive capacity is not expressly stated, it is certainly implied in Baker's statement. This is evidently the Nernst-Thomson rule in a slightly modified form. In view of the work of Kahlenberg and Lincoln,[1] Lincoln,[2] and Schlundt,[3] which proved that the Nernst-Thomson rule did not even hold qualitatively, much less quantitatively, it is surprising that Baker should attribute the ability of a liquid to induce the reaction in question, to its specific inductive capactiy.

In Table I there has been included the dielectric constants of the various liquids as given in the Landolt-Börnstein Tabellen (1905). A prediction from the specific inductive capacity would lead us far from the truth, if it is maintained that any liquid possessing a high dielectric constant will produce a reaction. For nitrobenzene, with a value of 36.45 and acetyl chloride (25.3) have no effect on the gaseous mixture, whereas either should act even better than the alcohols. Or, if the "rule" is modified to read "if any action occurs it will be caused by a liquid of high specific inductive capacity," then ether, which has a low value (4.3) forms an important exception. Nor do the esters employed have very high values; but the accuracy of the observations upon them in this investigation might be questioned, on the score of the ready decomposition of esters upon distillation. Moreover, it is not quite clear just where to draw the line between a high and a low dielectric value. Cases in point are ethyl chloride (6.29) and ethyl disulphide (7.2).

That association in the liquid state cannot be a determining factor is clearly seen from the last column of the table. Most of these values are taken from the work of Ramsay and Shields. Liquids, such as ether and benzaldehyde, which are unassociated, and methyl ethyl ketone, which is slightly so if at all, are capable of affecting the mixture. Moreover, Baker found that liquid sulphur dioxide, also an unassociated liquid, will induce the change.

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[1] Jour. Phys. Chem., 3, 12 (1899).
[2] Ibid., 3, 457 (1899).
[3] Ibid., 5, 157 (1901)

Of late years there have been included under the term "catalysis," many phenomena of apparently different character. So the influence of traces of moisture or other substances upon chemical reactions has been commonly ascribed to catalytic action. But this is no satisfactory explanation of the process, for it does not help us at all in gaining a clearer insight into the mechanism of chemical change. What essential difference is there between the action of ammonia and hydrochloric acid gases in the presence of a trace of moisture, and the neutralization of ammonium hydroxide by a solution of hydrochloric acid? In the latter case water is just as much a catalyzer as in the former. A satisfactory theory of catalysis will apply equally well as a theory of solutions and *vice versa*.

From the study of reactions involving pure substances, there has arisen the idea that pure compounds cannot react except in the presence of a suitable additional reagent. The function of the solvent, according to the theory of electrolytic dissociation would be to separate the reacting substances into ions. However, Kahlenberg[1] has demonstrated that instantaneous actions may proceed in non-ionizing media. Armstrong too, has always contended that the function of the solvent was not to dissociate but to associate; not to separate substances into ions, but to build them into complexes. The following quotation from one of his papers gives Armstrong's[2] views on the subject.

"Regarding the problem from the standpoint of Faraday's electrolytic studies, and in view of the well-known observations of De la Rive, Brereton Baker, Cowper, and Dixon, I assume, however, that no two molecules can interact directly; that in all cases of chemical interchange (including electrolysis) the necessary *slope of potential* can only be provided by the inclusion of the interacting substances in a triple or tripartite conducting system."

The assumption that "no two molecules can interact

[1] Jour. Phys. Chem., 6, 1 (1902).
[2] Proc. Roy. Soc., 81, 83 (1908).

directly" is not warranted by the facts as we know them at present. Even in the case of the system, hydrogen sulphide and sulphur dioxide, Baker maintains that liquid sulphur dioxide can induce the reaction.

But the question of the possibility of the direct interaction of two molecules, in no way affects the idea that the solvent enters into combination with the solutes in cases of chemical action. On this basis, the liquid would form intermediate compounds with the hydrogen sulphide and sulphur dioxide, which subsequently would rearrange to produce the final products. Now, as to the nature of these intermediate compounds, it is not necessary that they conform to the law of definite proportions. Slowly the idea of compounds in varying proportions is gaining favor. Nor is it to be expected that the intermediate compounds be prepared step by step in the order of their occurrence during a reaction, for our methods of isolation of substances are such as would continually change the composition of the intermediate compounds.

It is therefore assumed, that the liquids which induced the reaction between hydrogen sulphide and sulphur dioxide, entered into a loose chemical combination with the gases; that in those cases, in which the organic liquid was unable to initiate the chemical change, no such loose combination occurred. Many examples of the action of hydrogen sulphide or sulphur dioxide upon the organic liquids employed in this investigation are recorded in Beilstein. The contention is not made that these compounds are intermediary in the reactions reported in this paper. They are inserted merely to emphasize the possibility of chemical combination between the gases and the liquid. Nitriles unite with hydrogen sulphide to form thioamides, $CH_3CN + H_2S = CHCSNH_2$. Aldehydes exchange their oxygen for sulphur. $C_6H_5CHO + H_2S = C_6H_5CHS + H_2O$. Addition compounds may also form.

$$RCHO + H_2S = RCH\begin{matrix}OH\\SH\end{matrix}.$$

Both aldehydes and ketones form addition products with salts of sulphurous acid, so it is likely that they would

possess some attraction for sulphur dioxide. In fact, Bössneck[1] has shown that sulphur dioxide enters into loose combination with acetone. Aldehydes are capable of similar action. Carvone yields a well defined crystalline product with hydrogen sulphide $2C_{10}H_{14}O.H_2S$. In the case of the alcohols, it is clearly the specific properties of the hydroxyl group that come into play. Whatever rôle is assigned to water, would apply equally well to the alcohols.

Summary

The main points contained in this paper are:

1. An apparatus has been devised by means of which the effect of organic liquids upon the interaction of the gases, hydrogen sulphide and sulphur dioxide, could be determined.

2. Water in its ability to accelerate chemical change is in no way exceptional or unique, since other liquids have been found that have the same power. Of those investigated, the following induce the reaction: ethyl, isobutyl and isoamyl alcohols; acetone; methyl ethyl ketone; acetonitrile; propionitrile; valeronitrile; benzyl cyanide; methyl benzoate, propyl acetate; isobutyl acetate; ether; benzaldehyde and carvone.

3. Some liquids are unable to accelerate the action. Of the liquids investigated, the following produced no action: carbon bisulphide; ethyl disulphide; benzol; amylene; chloroform; carbon tetrachloride; ethyl chloride; acetyl chloride; benzoyl chloride and nitrobenzene.

4. There is no rigorous parallelism between the specific inductive capacity or the association of the liquid solvent on the one hand and its ability to induce action on the other.

5. A rational explanation of the phenomena lies in the view that chemical action occurs through the formation of intermediate compounds.

This investigation was carried out under the supervision of Professor Kahlenberg. I take this means of acknowledging my obligations for his interest in the work, and also for his generosity in placing at my disposal his private collection of chemicals.

University of Wisconsin,
June, 1910

[1] D. R. Pat. 47093, Ber. chem. Ges. Berlin, 22, c; 303 (1889).

ON THE TRANSFERENCE AND TRANSFORMATIONS OF ENERGY WITH APPLICATIONS TO THE THEORY OF SOLUTIONS

BY M. M. CARVER

To the practical, working chemist the conservation of mass, or matter, is the basis of all of his operations and deductions. He assumes as a matter of course, that if no material substance has entered or left his apparatus, he still has his original substance matter intact. And while in many chemical processes he may not be able to comprehend the exact state of the material present, he nevertheless relies on his fundamental principle; the material is present in some form. Now those characteristics of conservation, so fundamental in the case of matter, must hold also in the case of energy, for it also is conserved, or is constant in amount so long as none enters or leaves a given inclosure or system of bodies. From the principle of conservation it follows of necessity that changes in amount of energy in a given system of bodies, or even in the different parts of the same system, can be due only to the transference of energy from one point to another.

The object of the present paper is to attempt to correlate certain facts and to establish some criteria by means of which the direction of transfer of energy in certain cases may be recognized; and from the direction of transfer, to deduce a rule that shall aid us in forming a judgment of changing energy states in certain transformations and processes with a view to obtaining a better understanding of the energy relations of the phenomena we observe.

In consequence of the transmission of energy by means of radiation and conduction through communicated motion, the study of energy transfer becomes more complicated and difficult than the transference of matter; but this difficulty furnishes no valid objection to making a careful analysis of the conditions and mechanism of transfer with a view to establish-

ing the general laws and underlying principles of energy transfers.

While the principle of the conservation of energy may rightly be claimed to rest on an experimental basis, it is only partially expressed in the first law of thermodynamics, and its strongest proof is found in the fact that to assume its truth always leads to verifiable, or consistent, results. Hence if we can in a somewhat similar manner also extend and generalize the second law of thermodynamics and find that we are led to results consistent with our limited experience we may then use such extension to aid us in those cases where our experience is insufficient to furnish a satisfactory basis for a conclusion.

Suppose we assume as the natural law underlying the second law of thermodynamics, that:

In an isolated system all spontaneous, naturally occurring, processes are essentially equilibrating processes during which energy passes from points of higher to points of lower intensity of the type undergoing transfer, tending to produce a state in which each element of space gives out as much energy as it receives.[1]

The foregoing statement may be used as a basis for a more general enunciation of the second law of thermodynamics than that originally due to Clausius, as follows:

All transformations into potential forms of energy, like the doing of mechanical work, take place during the transfer of some type of energy from points of higher to points of lower intensity of the type undergoing transfer.

It should be observed that it will be necessary to distinguish between states of equilibrium and steady states not in equilibrium, like a battery circuit giving a steady current, but in which a chemical transformation is taking place at a *steady rate.*

The first most obvious objection to the above statement

[1] Since the above statement was formulated I have found a somewhat similar statement *partially* embodying the same idea in Professor Reeve's book on "Energy," p. 204. His point of view is otherwise, however, quite different.

of the second law of energetics as a working rule is, that in addition to discontinuities in intensity during transformation of type, we have no general criterion of energy intensity except in the case of heat. Notwithstanding this objection we shall find that in another important class of cases a criterion as to direction of transfer can be established, while it is already established and accepted in the case of the most universal form of energy, heat. The notions, intensity and direction of transfer, may be made mutually to aid each other; we may establish either from a knowledge of the other when known. We may then use the information so gained in cases where there would otherwise be doubt. Thus we may in many instances gain important information as to intensity of energy from knowing the direction of transfer, the direction being determined from dynamical considerations more general than the special instance under observation. For instance, we know from dynamical principles that when mechanical work is done by the action of a force producing motion of its point of application, energy is transferred, or transmitted, in the direction of the resultant motion, only by a push, a compression, or a pressure, etc., while a pull, or a tension, transmits energy in a direction opposite to the direction of the motion produced by the tension. Example; the transmission of power by belting and the doing of work by means of cords and strings.

Since fluids are not susceptible to appreciable tensions or pulls, but to pressures only, a spontaneous, natural, transfer of matter in the form of fluid indicates a transfer of energy in the direction of the transfer of material and from points of higher to points of lower intensity of energy. If the motion of the fluid is opposed by friction, heat is distributed along the path of motion. If the motion is resisted by attractive forces, work is done against the forces. By the first law of motion (Newton) the motion will continue until the energy due to the motion is absorbed in some manner and, in the absence of external effects, the absorbing space gives out as much energy as it receives. We then have a state of equilib-

rium. But the absorption and disappearance of energy of one type always necessarily involves the appearance of an equivalent amount of some other type. (The principle of conservation.) Hence we can confirm the above generalized statement of the second law of energetics by the following reasoning:

It is shown by Nernst[1] that instead of accepting the second law as limited by Clausius, it may be expressed more generally as follows:

"All spontaneously occurring natural processes may, by appropriate devices, be utilized to do a finite amount of mechanical work." Accepting this as a fact of experience and combining it with the first statement that all spontaneously occurring processes in an isolated system are essentially equilibrating processes and we arrive at the conclusion that:

In an isolated system, work or potential energy, appears only during the spontaneous transfer of energy from points of higher to points of lower intensity, accompanied by an equilibrating of the various energy intensities. Whether work be done or not depends upon whether or not the energy stream has had a portion, or, in the limit the whole, of the energy undergoing transfer diverted into the particular form called work, such as overcoming attractive forces as lifting a weight, etc.

From the above stated point of view it is evident that the particular form of energy to us the most important, *i. e.*, work, is but an incident, a mere episode, as it were, in the ceaseless ebb and flow of the energy tide. Every form, however, of potential energy, such as mechanical work introduces a discontinuity in the intensity of the energy diverted from the course of its natural flow; for the work in disappearing may be transformed into energy of an intensity bearing no functional relation to the intensity of the energy from which the work was originally derived. But the law of conservation enables us to assert that notwithstanding the discontinuity in the intensity of energy in passing through the potential form, the intensity

[1] Theoretische Chemie, 6th edition, 18 (1909).

is nevertheless inversely proportional to the redistribution, or extensity, of the retransformed energy. For if a quantity of energy, Q be represented by the product of two factors, extensity E_x and intensity I the second law of energetics asserts that

$$Q = E_x I = W + Q'$$

where W represents the transformed and Q′ the transferred energy. If W be transformed back into energy of the same type, we must have

$$E_x I - E'_x I' = Q' \geq o.$$

This is a more general statement than that embodied in the entropy function,[1]

$$\sum \frac{d H}{T} \geq o$$

for the latter refers to only one type of energy while the other asserts that transformations are dependent on transfers and that there must necessarily (except ideally) be some energy transferred, for transformations occur only during transfer. In addition this equation shows the discontinuity in the intensity factors I and I′ which evidently bear no functional relation to each other so long as the extensities are independent and arbitrary.

The foregoing may be taken as a concise outline of a point of view. If it is in opposition to, or inconsistent with, any well-established thermodynamic facts I have failed to observe them. Indeed many of the leading facts of thermodynamics seem to follow directly as a consequence from the above assumptions. Without at present attempting a systematic comparison of the facts of thermodynamics with the suggested assumptions, perhaps the best way to present the subject as a

[1] "It would be absurd to assume that the validity of the second law depends in any way on the skill of the physicist or chemist in observing or experimenting. The gist of the second law has nothing to do with experiment; the law asserts briefly that *there exists in nature a quantity which changes always in the same sense in all natural processes.*" Planck, Thermodynamics, translated by Ogg, p. 103.

whole without detailed analysis, will be to illustrate by a series of statements how some of the fundamental facts of thermodynamics follow by simple non-mathematical deduction from the above general assumptions. But absence of conflict is not sufficient. Not only should we expect the general to include the special, but a general form is an unnecessary complication if it does not enable us to take a forward step and include phenomena that were previously isolated.

1. Energy, like matter is conserved, and again like matter may vary in amount per unit volume or space. The variation of matter per unit volume is recognized as change in density. The variation of energy per unit volume is expressed as variations in intensity.

Dropping the use of analogies, for they are only analogies, we may proceed:

2. All natural processes taking place spontaneously in isolated systems are essentially equilibrating processes during which each type of energy, independently, tends to become uniformly distributed, by the passage of energy from points of higher to points of lower intensity.

3. During a transfer of energy due to the equilibrating process, transformations occur; (*a*) by distributions along the path producing molecular motions; (*b*) by overcoming attractive forces internal and external; (*c*) by communicating motion to masses against inertia or other resistance. All spontaneous transfers of energy in an isolated system must then result in an equilibrating redistribution of energy either molecular or molar, or in a partial redistribution and a partial transformation into potential energy constituting work either external or internal or both.

4. Each type of energy can in general be equilibrated by intensities of its own type and by some potential form or forms; but different types may have the same potential form and consequently may be equilibrated by a common potential. Hence actual equilibrium may co-exist with great energy heterogeneity.

5. If a transfer of energy of any type results in equilibrium without change of type the process is finished, the incident is

closed; there remains no latent possibility that that particular redistribution can be made to take place again so as to produce a potential form, *i. e.*, do work. (Irreversible processes.)

6. Ability to control the rate of transfer of energy without lowering the intensity necessarily implies the ability to equilibrate one intensity against another. Hence, if the equilibrating intensity be of a type susceptible to control the transformation of the two types from one into the other may be made to take place slowly in either of two directions with but slight lowering of intensity of either type. (In the limit, no lowering.) Therefore if an energy transfer can be made to take place sufficiently slowly by equilibrating of intensities, energy that would otherwise be transferred may be transformed with a minimum of loss by transfer. (Reversible processes.)

7. In all actual redistributions of energy due to spontaneous motion by which energy is transferred from points of higher to points of lower intensity, some difference in intensity must exist or transfers will cease. Therefore transformations (which take place during transfer) are never complete; some energy necessarily being transferred and the remainder transformed. (Law of entropy.)

8. An isolated energy system, free from external action, relatively at rest, and occupying a constant volume, can exist only with one-half of its energy kinetic and one-half potential. (Clausius' virial.)

This last statement follows immediately from the first and third laws of Newton and is necessarily true in general unless strain may exist independent of motion in which case we can assert only that the kinetic energy cannot exceed the potential energy which reaches a minimum when it equals the kinetic energy of the system. As applied to a fluid system not subjected to external stresses, as in a free liquid, it merely specifies a condition of equilibrium which is evident from general principles; but those who require an analytic proof will find it in Clausius'[1] virial:

[1] Phil. Mag., [4] 40, 122 (1870).

Each of the above statements might be made a text for a more extended discussion and comparison with experimental facts; but even in their present abridged form they will serve to show that the proposed extension of the second law of thermodynamics to include all kinds of energy transfers is, to say the least, not inconsistent with its present narrower interpretation. In addition, the proposed extension throws a light on the significance of irreversible and reversible processes and on entropy that cannot fail to be helpful in the application of the second law of energetics to the phenomena of solution. The facts seem to indicate that the phenomena of solutions are in a class by themselves and require a fundamental treatment. The thermodynamics of gases cannot be made to explain fundamental characteristics not found in connection with the phenomena of gases. Of course there are resemblances but there are also differences. The resemblances are, however, superficial while the differences are fundamental. The warrant for this last statement, it is expected, will be evident from the result of a study of a few of the fundamental *experimental* facts of solutions. The first of the following examples will be discussed in more detail than the remainder because it illustrates simultaneously co-existing different types of energy and the conditions of their equilibrium and transfer as well as an instructive reversible transformation into work. We shall find the study much facilitated by the application of the rule that a spontaneous transfer of fluid matter indicates the relative energy intensities, as well as the direction of transfer of the energy. Of course the rule may be objected to but the objector may find it difficult to explain how the matter undergoing *spontaneous* transfer manages to leave its intrinsic energy behind.

Application of the Preceding Principles

If two vessels, one containing a volatile liquid and the other a solution of a non-volatile solid in the same liquid, be placed side by side in an inclosure from which the air is exhausted, the volume of the solution will increase at the ex-

pense of that of the pure solvent so long as the temperatures of the liquids in the two vessels are equal. From the well-known relation of vapor-pressures to temperatures, we know that if the solution be at a certain temperature, somewhat above that of the pure solvent, the vapor of the solution will be in equilibrium with that of the pure solvent. The two liquids will then possess different temperatures and are consequently not in thermal equilibrium, yet their vapors are in equilibrium, we say, because they exert equal pressures; but heat will pass from the warmer to the cooler vessel both by radiation and conduction if the vessels are in thermal communication. If the temperature of the solution be higher than this equilibrating temperature, both radiant heat and vapor pass in the same direction, *i. e.*, from the solution to the pure solvent. If the temperature of the solution lie between the equilibrating temperature and the temperature of the pure solvent, radiant heat and vapor pass in opposite directions. If the solution be cooler than the pure solvent both radiant heat and vapor pass from the pure solvent to the solution. Such are the experimental facts with a few obvious deductions from the facts. In addition, experimental facts relating vapor pressure to altitude, show that if the temperatures of the two liquids be the same, the vapors may be equilibrated by a difference in level of the two containing vessels—the solution occupying the higher level. If too high, vapor will pass from the solution; if too low, vapor will pass to it and be condensed. Other equilibrating devices employing semi-permeable partitions need not at present be considered, as they were discussed at some length in a former paper.[1]

The point to which special attention is called is the co-existence of two types of molecular energy—heat and the ability to form vapor—either of which may be equilibrated independently, but not simultaneously without introducing a third element, or potential, a difference in level. With a properly selected difference in level both temperature and vapor pressure may be simultaneously equilibrated. But

[1] Jour. Phys. Chem., 14, 260 (1910).

with the vessels at the same level vapor equilibrium can be attained only when the solution is at a higher temperature than the pure solvent; and in producing this difference of temperature—thermal communication being prevented—the transferred vapor acts in the double capacity of lowering the temperature of the pure solvent and elevating that of the solution. If communication of heat be prevented the vapors will reach equilibrium by producing the necessary difference in temperature.

The ability of the pure solvent to raise the temperature of the solution at the expense of the heat in the pure solvent indicates the presence of "free energy"—the ability to do work—the energy being supplied by the pure solvent and being absorbed by the solution. Instead of being transferred to and absorbed by the solution, producing heat, it may be transferred against gravity and made to do gravitation work. For details of a reversible process of accomplishing this a former paper may be consulted.[1]

This peculiar example—a transfer of molecular energy, not heat, producing either heat or work at will is more nearly analogous to a battery circuit containing an electric motor than it is to gas expanding into additional solvent like a gas expanding into a vacuum. If the motor be allowed to run and lift a weight, gravitation work is done; if stopped, the entire energy is transformed into heat. At a certain definite speed of the motor, both the transfer of electricity and transfer of chemical material may be equilibrated; at a still higher speed both may be reversed in direction by the doing of external work. If a reference to a gas be used at all to illustrate the redistribution of the energy, a better illustration is afforded by Joule's first experiment. Consider two equal masses of the same gas occupying different volumes, *i. e.*, subjected to different pressures. If they are placed in thermal communication they will come to the same temperature. Now if we have equal masses in the two portions we have equal numbers of molecules and each molecule, if we accept the

[1] Loc. cit.

kinetic theory of the molecule, possesses the same average kinetic energy of translation, so that the two portions of gas represent equal amounts of energy. The real difference between the two portions is found in the energy per unit volume, or intensity. Together, the two parts constitute an energy system capable of producing a difference in temperature in the parts of the system or of doing external work instead. In this respect, such a gaseous system is very similar to a system composed of a solvent and solution such as we have been considering. The resemblance extends even to balancing the free energy by a temperature difference; but the free energy in the two systems is quite differently related to their respective systems. In the one we have a homogeneous gas, the equilibrium of the system being disturbed by, and the free energy arising from, a difference in externally applied pressure. In the other we have a compound liquid system in which the equilibrium is disturbed by, and consequently the free energy arises from, the presence of a non-volatile substance dissolved in one portion of an otherwise homogeneous liquid. The transfer of material from the pure solvent to the solution spontaneously, proves that the energy per unit volume of the pure solvent exceeds that of the solution when the temperatures are equal; therefore the free energy of such a system resides in the pure solvent during the spontaneous transfer of which, to the solution, work is done. Strictly speaking, the free energy in the sense of ability to do external work, is a function of the system and not of either constituent alone, but may be said to be due to a disturbed equilibrium in consequence of which material is transported spontaneously from one part of the system to the other. The maximum quantity of work which may be done by such a system may be calculated by either of two processes and yields the same result when ambiguities are removed. The method by equilibrated vapors was given in the paper referred to above, but the same numerical results, when correctly interpreted, may be obtained by "osmotic" methods which may be termed the static (because dealing with pressures, or forces),

method as compared with the above which might be called the kinetic. It may not be amiss to offer, at this point, a few reflections on the above distinctions—the static and kinetic.

The first law of Newton is really dual and opens the way to the two different methods of viewing things, the static and kinetic. (*a*) Matter at rest remains at rest, etc. (*b*) Matter in motion remains in motion, etc. The fact is, we are really dealing with two aspects of the same thing, energy, or, more properly speaking, matter in motion. (This last phrase shows the personal predilection of the writer.) But we should all recognize the fact that pressure may produce motion and motion, pressure as illustrated by the phenomena of gases. In many instances it is as difficult to determine which is antecedent and which consequent as in the proverbial case of the egg and the fowl. We may start from either point of view and obtain results that are consistent with themselves and with our general experience. Since, however, the kinetic view of fluid matter has so enlarged our conceptions of the activities and processes found in Nature, it seems but reasonable to postulate that the phenomena we observe arise from interchanges of matter in motion. Hence the proposed generalized second law of energetics is merely another way of saying that nothing can happen while everything is at rest.

As the history of science proves, either of two hypotheses, or theories, may sometimes equally well account for all the known facts until the material for a crucial experimental test enables us to decide which of the two best represents the widest range of facts. The rival views inevitably lead *to different interpretations of the same fact* and experiment must be appealed to to decide between them. In the present instance the osmotic theory, as opposed to what we may call the chemical theory, requires that when work is done by a solution due to the expanding solute, it must be *cooled* in consequence of the external work done by the expanding solute.[1] The experimental facts of the relation of vapor

[1] Nernst, Theoretische Chemie., 6th Ed., 147 (1909).

pressures to temperature require that the solution be *warmed* in order to produce equilibrium of the vapors. Hitherto the relation of the vapor pressures to the ability of a solvent-solution system (for brevity) to do external work was not fully recognized; but since the maximum work by a reversible isothermal process may be obtained by the interaction of the vapors alone[1] it is evident from the principle that work or potential energy, is produced only by transformation occurring during transfer of energy, that the work actually done by the system must merely diminish the molecular energy, or heat, transferred from the pure solvent to the solution. This means that warming the solution until the equilibrating difference in temperature is produced should absolutely prevent the doing of work by the system because it prevents the transfer of energy and material which is the prerequisite to doing work. This deduction from the experimental evidence is easily tested experimentally. It has been proven frequently that a certain difference of temperature will equilibrate the vapors and prevent transfer of vapor; the same difference in temperature will undoubtedly also prevent the transfer of liquid material through a semi-permeable membrane.

The characteristic features of a solvent-solution system are that it may be equilibrated in three different ways, (*a*) by a temperature difference, (*b*) by a difference in external pressure, (*c*) by a difference in level equivalent to the difference in pressure. This indicates plainly that the system will produce any one of the three differences when the other two are prevented, since all processes tend to produce equilibrium, ultimately. The system does work because the solution is cooled, not the converse. By the second law, the transfer of heat is antecedent, the doing of work consequent. The doing of work can be prevented by preventing any transfer of heat; but if the vapors are in communication the solution will become warmer than the adjacent pure solvent.

Query. What is the character of the energy in such a

[1] Jour. Phys. Chem., 14, 260 (1910).

system? and where does it originate? It is not heat that may be indicated by a thermometer or a pressure that may be measured by a manometer; its transfer *produces* these characteristics of free energy. It is, from the evidence, a distinct type that may undergo distribution without change of type (irreversibly) or may, during transfer, be transformed producing a temperature difference or do work while producing a less difference in temperature. If it produces a temperature difference it is, of course, distributed as heat and follows the thermodynamic laws found to hold in such distributions; but there is a persistent transfer of energy when both the temperatures and the externally applied pressures are uniform throughout the system. It must then differ in type from heat, for heat transfer is accompanied by a difference in temperature. Otherwise, except as to temperature characteristics, it strongly resembles the molecular motion called heat and has a heat equivalent.

Its origin is interesting and curious for it seems to originate in the potential energy (chemism?) of solution just as heat originates in the chemism of combustion.

When coal is burnt it can produce a perfectly definite amount of heat which may be distributed as heat, irreversibly, or may produce a difference in temperature which may be utilized to do work, the heat not being entirely distributed so long as any temperature difference, or work, remains in existence. The production and distribution are entirely distinct quantities; they may occur simultaneously or consecutively.

When a solute is dissolved, a perfectly definite amount of energy is set free and may be distributed at once by indefinite dilution, or, a concentrated solution may be diluted and additional work obtained during and by the process of dilution, but the distribution of the energy is not complete until the solution is infinitely diluted. The energy set free and the work obtainable by dissolving unit mass of a substance is equal to $mg\,h$ where m is the mass of the solvent and h is the height necessary to equilibrate the difference in vapor-ten-

sions.[1] If h varies, m varies inversely, so that the total work *is independent of the quantity of solvent used*, so long as the solution is complete, and is just sufficient to lift the entire mass of solvent to a height h against gravity. It is evidently a definite potential and may *be interpreted* as indicating *a definite chemical union* uninfluenced by the excess of the solvent, just as any excess of air does not affect the quantity of heat during complete combustion, merely the distribution and temperature. The energy obtainable by solution is entirely independent of whether work is done or not just as in the case of combustion. It may be carried out so as to obtain work, but while the work exists as work, the molecular energy produced by the solution remains incompletely distributed.

The subject can be illustrated more strikingly and the significance of redistributions of matter and energy, and the resulting equilibrium shown better by two specific cases.

Consider a piece of charcoal in a jar of oxygen. If the charcoal be above a certain temperature the system will not be in equilibrium and the process called combustion takes place with the result that the carbon is uniformly distributed throughout the oxygen and the oxygen throughout the carbon. The resulting heat can be used to do work; but if the combustion be conducted in the open air a simple irreversible distribution takes place.

An exact parallel is seen when sugar is dissolved in water except that instead of a rise of temperature there is a drop, otherwise the redistribution takes place until the sugar is uniformly distributed throughout the water and the water throughout the sugar. During the process a definite amount of work is possible, but the energy distribution may take place either reversibly, or irreversibly without change of type. If reversibly, work may be done as during dilution, when part of the energy undergoing transfer may be transformed into work. If no mechanical work be done it may be entirely transformed into heat and be distributed as such, or, be

[1] Jour. Phys. Chem., 14, 263 (1910).

distributed *without change of type* directly without the production of heat, as on direct dilution by adding additional solvent to a dilute solution.

For my part, I do not see how to identify the type of energy distributed in the case of the sugar and water with the type of energy called heat in the case of the carbon and oxygen. The conviction is forced on my mind that each separate substance represents a distinct type of energy tending to uniform distribution irrespective of every other type as is so plainly manifested in the case of gases.

To those who have thus far followed the deductions from the experimental facts as interpreted by means of the generalized second law of energetics applied to the phenomena of solutions its great utility should be apparent. We have without recourse to the phenomena of osmosis isolated the hidden energy and traced it to a source, which, by the writer at least, has been hitherto unsuspected. And while osmosis, as such, is found not to be the source of the energy, the energy is always present in the phenomena of osmosis, thus indicating that there was ample warrant for the conclusions of those who regarded osmotic pressure as representing an energy otherwise unidentified and which certainly is neither heat nor work but can be transformed into either. The regular thermodynamic treatment fails to do more than to express the conditions of equilibrium in terms of an entropy function and the ordinary variables of thermodynamics. But little insight into the energy relations is thus obtained; and energy relations are all-important to a rational comprehension of the phenomena. However, Planck distinctly states that the free energy of a solution after mixing with additional free solvent is less than the free energy of the materials existing separately, before mixing,[1] but he fails to give any indication that this is due to the presence of a distinct type of energy causing a transfer *from* the pure solvent *to* the solution. Since osmosis and osmotic pressure constitute its most characteristic phenomena, osmotic energy would not seem inappropriate but it could not approp-

[1] Loc. cit., p. 204.

riately be termed "the energy of a dissolved substance" although the energy arises from the presence of a dissolved substance but only as it constitutes an "energy sink." Properly speaking it should be called solution energy.

We have traced the solution energy that gives rise to the phenomena of osmotic pressure and osmosis to the potential energy of the solute set free by its union with a solvent, which union gives rise to a peculiar type of energy just as the union of carbon with oxygen gives rise to the peculiar type of energy called heat. Each type of energy may be transformed into work by processes applicable to the special type, but each necessarily involving the transference and partial distribution of the energy set free as a condition precedent to the transformation. The transference of solution energy is conditioned on dilution as the *sine qua non* of distribution during which mechanical work may, or may not, be done just as in the case of heat, work may or may not be done during distribution. The doing of work during dilution is conditioned on a depressed state of a solution as compared to the energy state of the pure solvent; for the transfer takes place spontaneously from the pure solvent to the solution. It remains to reconcile this latter deduction with the deduction from the kinetic theory that the average energy per molecule of a solution is the same as that of the solvent at the same temperature. That the two conclusions are not necessarily in contradiction is shown by the fact that equal average energy per molecule holds also for gases at the same temperature, but that a difference in pressure confers on such a system free energy. Hence we may admit that the average energy per molecule is the same in both solvent and solution without necessarily admitting that the free energy is the same in both. The problem, then, is to determine, if possible, how the free energy of a solution can be less than that of the solvent while the energy per molecule remains unchanged.

As a preliminary, we may note that if the pressure of the vapor be taken as a criterion of free energy we can express the difference in the free energies in terms of a pressure, just

as in the case of two portions of a gas at different pressures. This pressure criterion may even be extended to the liquids as well as to the vapors by introducing the conditions of simultaneous dynamic equilibrium between the vapors and liquids, namely:

$$\frac{p_1 - p_2}{p_1} = \frac{P_1 - P_2}{P_1}$$

where p_1 and p_2 are the vapor pressures of pure solvent and solution respectively and P_1 and P_2 are the intrinsic pressures of the respective liquids.[1] The transfer of material, whether vapor or liquid will take place spontaneously if not prevented, from the higher to the lower pressure, and thus introduce a process expressible in terms of "pressures" during which external work may be done. In terms of energy, however, since "free energy" is merely another expression for ability to do work, which ability disappears entirely when the difference in vapor pressures disappears either by dilution or by a temperature difference, we may without doubt assume that the average molecular energy per molecule, E_1 or E_2 of the material which supplies the vapor, is proportional to the pressure p_1 or p_2 of the vapor which it supplies. Therefore

$$\frac{E_2}{E_1} = \frac{p_2}{p_1} = \frac{P_2}{P_1}$$

where the subscript 1 refers to pure solvent and 2 to the corresponding solution.

Suppose N molecules of solution to consist of n molecules of solute and N–n molecules of solvent; the total free energy being E. The average free energy per molecule of solution will be $E/N = E_2$ and of the solvent in the solution (since the non-volatile solute furnishes no vapor), $E/(N-n) = E_1$ say. The ratio $E_2/E_1 = (N-n)/N = p_2/p_1$ whence

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}$$

Raoult's experimentally observed law. Since the assumptions

[1] Loc. cit., p. 265.

lead to an experimental law, we may regard them, not only as warranted, but as indicating an interpretation of Raoult's law.

The previous deduction, however, throws no light on the constitution of the molecule. The N molecules of solution are regarded as formed from n molecules of solute and N–n molecules of solvent; their actual number does not enter into the result. In order to obtain information on this point it will be necessary to proceed differently; we must consider the changes that take place on solution.

When a solid, non-volatile solute is dissolved, three cases may arise: (*a*) a rise in temperature: (*b*) a fall in temperature: (*c*) no appreciable temperature change. Let us consider the last case first; a detailed consideration of the others will be found unnecessary.

The absence of temperature change does not imply the absence of chemical action. It must be interpreted as meaning merely that the work done during solution is just equal to the work done on the solute in changing it from a free solid to a solute. Energy existed in potential has disappeared and in another form, has been transferred to the solute. If no energy enters or leaves the system and the solvent and solute undergo no temperature change, the entire result consists in changing the state of the solute without taking any heat from the solvent. If we accept the kinetic theory, each molecule of the solution has an average energy equal to the average energy per molecule of the original solvent and to the molecules of free solvent in the solution when the temperatures are equal; but has the number of molecules changed? That is the question.

In this connection it is important to remember the fundamental bearing of the second law of energetics that it is only during transfers of energy that transformations take place. We have here a transfer of energy and we may, or may not, have a change in type due to transformation during the transfer. It seems to me that the evidence indicates a definite change of type; but this evidence may be considered later.

It is evident on consideration that the separation and distribution of the molecules of the solid solute can be accomplished only by the molecules of solvent entering between the molecules of solute; consequently the attractive forces of solvent for solute must exceed the attraction of solute for solute. Or, the union of the solvent with the solute can be comprehended from the energy viewpoint only by supposing a decrease in chemical potential with a corresponding production of heat, or a release of free energy, or both. If we consider the relative volumes of the solute before and after solution, the energy of its molecules and their separation against their molecular attractions, the energy required to dissolve it is comparable with the energy required to gasify it. Since we are supposedly dealing with an isolated system this increase in energy all comes from energy supplied by the solvent. We may therefore suppose that the total energy supplied by the solute is small as compared with the total energy supplied by the solvent in a moderately dilute solution. From statement 8 (Clausius' virial) we may conclude that the kinetic energy in a free liquid is proportional to the absolute temperature T. Therefore if E represents the total energy of N molecules of solvent the average energy per molecule of the solvent is $E/N = E_1$ (say). Likewise, the average energy per molecule of the solution will be $(E + e)/N' = E_2$. Therefore

$$\frac{E_2}{E_1} = \frac{(E+e)}{N'} \times \frac{N}{E} = \left(1 + \frac{e}{E}\right)\frac{N}{N'} = \frac{T_2}{T_1}.$$

Now since e is small in comparison with E, $\left(1 + \frac{e}{E}\right)$ approximates to unity, and since T_2/T_1 is supposed to be nearly unity N/N' must also be not far from unity. When T_2 is larger than T_1 N', the number of molecules of solution, may be actually less than N_1 the original number of molecules of pure solvent.

As the observed lowering of the energy of a solution is apparently of such a nature that the thermometer does not show it (for at least one phase of the energy is lowered even

when the temperature is not lowered) the temperatures T_3 and T_1 probably do not correctly represent the relative energies of the solution and pure solvent. If *all* the energy due to the union was transferred in the form of heat and none of it transformed, the temperature T_2 of the solution should be higher. But if the energy transferred during solution be partly transformed into a subtype—a molecular potential type analogous to work—in the doing of which heat disappears, the heat generated partly disappears and the temperature produced is less than we should otherwise expect. Therefore the estimate that

$$\frac{E_3}{E_1} = \frac{T_2}{T_1} = \left(1 + \frac{e}{E}\right)\frac{N}{N'}$$

is probably too low and we should have instead

$$\frac{E_2}{E_1} > \frac{T_2}{T_1} < \left(1 + \frac{e}{E}\right)\frac{N}{N'}$$

so that probably $N' < N$.

Suppose on the other hand that we assume the absence of union and of energy set free during solution, and that therefore the energy E of the solvent is merely distributed among the $N + n$ molecules of the solution, the energy contributed by the solute being negligible. We should then have $E/N = E_1$ and $E/(N + n) = E_2$.

Whence

$$\frac{E_1}{E_2} = \frac{N + n}{N} = \frac{T_1}{T_2}.$$

If we test this formula with the results obtained with an aqueous solution of cane sugar we find that the solution of 1 gram molecule in a liter of water at 20° C should cause a drop in temperature of 5° C while the heat absorbed, as stated by Nernst is 800 calories, indicating a drop in temperature of less than 0.8 of a degree.

Hence when viewed from one side we are led to conclude that in a solution the number of molecules must be less than the sum of the molecules in the components; and from the other side that the observed temperature change is not suffi-

cient to indicate that an unchanged number of molecules was supplied with the requisite energy called for by the kinetic theory. These two indications moreover unite in confirming the deduction that the energy obtainable from dissolving a substance points to a definite chemical union with a decrease in the number of reacting molecules. In addition there are numerous other indications of a union of some sort between the solute and solvent. Osmotic pressure for instance, could be explained by a union of such a nature that the combined molecules could not pass the semi-permeable membrane.[1] It would also explain Pickering's experiment.[2] In simple cases like a solution of a non-volatile non-electrolyte "the action is as if each molecule of solute had removed from action one molecule of solvent." Let us then suppose that there is a loose but definite sort of molecular union between a solvent and its solute and see whether such assumption enables us to explain otherwise isolated phenomena.

Let x represent the molecular mass of the solute and y that of the solvent. Then $E_1 = {}^1/_2\, y\, u_1^2$ will represent the average energy of translation of the molecules of the solvent, if u_1^2 is the average square of the velocity of the solvent molecules. Let E represent the total kinetic energy of N molecules of solvent and e the total kinetic energy of n molecules of the solute which we will assume to be a non-volatile non-electrolyte. In accordance with the assumption, a molecule of solution will have a mass $(x + y)$ and an average energy of translation of $E_2 = {}^1/_2\, (x + y)\, u_2^2$ (say). The actual value of the average energy per molecule of the solution may be taken as lying between two limits. If we assume that the original energy e of the solute is negligible in comparison with the energy E of the solvent we get a lower limit. If we assume the kinetic energy of the solid solute before dissolving to be proportional to the absolute temperature and equal per molecule to the liquid solvent at the same temperature we will doubtless include the upper limit. Let us consider the lower

[1] Jour. Phys. Chem., 14, 651 (1910).
[2] Whetham: "Theory of Solutions," p. 97.

limit first. In this case the average energy per molecule will be the same after dissolving as before for the same amount of energy E is divided among the same number of molecules N so that $E_1 = E_2$ or, $\frac{1}{2} y u_1^2 = \frac{1}{2} (x+y) u_2^2$. If no molecular work were done during solution in separating the molecules of the solute there should be no temperature change during solution in consequence of such union for the mean kinetic energy of the molecules is proportional to the absolute temperature. The temperature change then should merely represent the disgregation work done during solution and this is generally indicated by a fall in temperature.

Now let us consider the second case in which the energy supplied by the solid solute is equal to the energy of the same number of molecules of solvent, still however, remembering that the number of molecules after solution is equal to the number of molecules of solvent. The energy now divided among the N molecules will be $E + e$ and the energy per molecule

$$\frac{E+e}{N} = E_1 + \frac{e}{N} = E_2.$$

The only effect of the increment e/N supplied by the energy of the solute will be to decrease the fall in temperature due to the disgregation work done by the solvent on the solute. Less heat then, will have to be supplied to restore the original temperature, if we include and take into account the energy supplied by the solute But entirely aside from the molecular work done which produces temperature effects it is seen that *there is a large amount of molecular work done in imparting kinetic energy to the solute that has no heat equivalent, for no fall in temperature results from the energy* $\frac{1}{2} x u_2^2$, *the entire kinetic energy imparted to the solute by the solvent.* If the two parts of the molecule, $\frac{1}{2} x u_2^2$ and $\frac{1}{2} y u_2^2$ had separately, before the union, had a surplus of energy it would have been given out as heat to the rest of the solvent and the fact would still remain that the energy $\frac{1}{2} x u_2^2$ is related to $\frac{1}{2} y u_2^2$ as though the energy of the part $\frac{1}{2} x u_2^2$ had been raised from zero by the fall of $\frac{1}{2} y u_1^2$ to $\frac{1}{2} y u_2^2$ without any

temperature change. The reason for this apparently paradoxical result is seen when we remember that the energy per molecule is independent of the mass of the molecule and hence that the work done by the molecule goes to change the mass of the molecule. Therefore that kind of molecular work does not change the temperature of the molecule that does it.

We are now in a position to see why the energy of the solution is depressed although the temperature is unchanged—why, although it has the same temperature and the same average energy per molecule as the pure solvent, the vapor persistently passes from the pure solvent to the solution and also why the liquid solvent passes through a semi-permeable membrane into the solution unless prevented by either a temperature, or pressure, difference. In this connection, however, it is necessary to remember that a transfer of energy is determined solely by relative intensities of the type undergoing transfer and is independent of total energies except as they affect equilibrium. Therefore the total energy in a solution may, or may not, be actually greater than in the original solvent, but if the intensity of any one type be less than the intensity of the same type at a nearby point and the conditions permit of transfer, energy of that type will pass spontaneously from the points of higher to points of lower intensity of that type and during the transfer work may be done. In the case of a solvent-solution system, the kinetic energy of the solvent in the solution is both depressed and divided beween the solute and solvent so that energy in the form of solvent passes freely to the solution where that type is depressed and diluted. The depression and dilution may be further analyzed from the equation

$$\tfrac{1}{2}(x+y)\,u_2^2 = \tfrac{1}{2}x\,u_2^2 + \tfrac{1}{2}y\,u_2^2 = \tfrac{1}{2}y\,u_1^2.$$

Here we have two types which united will equilibrate $\tfrac{1}{2}\,y\,u_1^2$ so far as heat is concerned when the temperatures are equal, but separately the part $\tfrac{1}{2}\,y\,u_2^2$ is less intense than $\tfrac{1}{2}\,y\,u_1^2$. Hence work may be done during the redistribution if conducted reversibly, or the type may be distributed directly and irreversibly without doing work or generating heat just

as in the case of heat. By infinite dilution the difference upon which the transfer depends disappears.

In addition we have the type $^1/_2\, x\, u_2^2$, generally a heavy molecule with a depressed velocity so that it forms no vapor nor is it able to penetrate semi-permeable membranes with the facility shown by the more active free solvent. This $^1/_2\, x\, u_2^2$ represents the "sub-type" of molecular energy the formation of which apparently takes no heat energy since it repays the energy it receives by adding mass to the molecule from which it receives its motion.

Résumé of evidence indicating a definite chemical union of solute and solvent.

(*a*) The definiteness of the energy, *mgh*, set free on solution.

(*b*) The energy set free indicates a union of molecules by which the number of molecules in a solution is less than the sum of the constituent molecules.

(*c*) The energy, as indicated by temperature changes, is not sufficient to supply an aggregate equal to the sum of the constituent molecules.

(*d*) The lowering of the energy of a solution although the temperatures of solution and solvent are equal.

(*e*) The doing of molecular work with a disappearance of energy without lowering the temperature.

(*f*) A union of the solute and solvent enables us to explain satisfactorily the depression of vapor and intrinsic pressures, hence osmotic pressure.

Finally the evidence and reasoning are not based on the kinetic molecular theory. The frequent references to the latter theory and the discussions generally were to show that the two views were not contradictory. They do, however mutually support each other.

State College, Pa.,
September 16, 1910

CRYSTALLIZATION THROUGH MEMBRANES

BY JAMES H. WALTON, JR.

In a previous communication[1] it was shown by the author that if a supersaturated solution or an undercooled liquid is divided by a membrane and a crystal is added to one part, crystals will form in the other part, the crystallization being transmitted *via* the membrane. This was found to hold true with aqueous supersaturated solutions of sodium sulphate, acetate, tetraborate, thiosulphate, potassium alum and lead acetate with parchment, collodion and gold-beater's skin. Similarly, undercooled water and thymol were used with collodion and gold-beater's skin.

An undercooled liquid of a type entirely different from any of those employed can be made by melting phosphorus in water to which a few crystals of urea have been added to facilitate the undercooling. A few experiments were carried out with this substance. The apparatus used is shown in Fig. 1. The membrane is fitted over the lower end of B, and this is slipped into A, which is made of a glass tube with a bore slightly larger than B. The phosphorus was melted in a beaker containing about 200 cc of water to which about 1 gram of solid urea had been added. The hot liquid was then poured into a separatory funnel, and the clear liquid phosphorus with a little of the urea solution was run into each of the arms A and B. On cooling to room temperature the phosphorus still remained liquid. Two series of experiments were made in which gold-beater's skin and sheet rubber (0.005 in. thick) respectively, were used as membranes. In neither case, however, was the crystallization transmitted through the membrane. The use of undercooled phosphorus is particularly interesting, differing as it does from some of the other

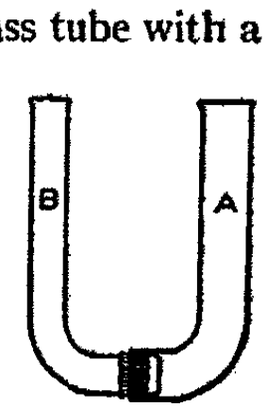

Fig. 1

[1] Jour. Phys. Chem., 13, 490 (1909).

substances used in the matter of speed of crystallization.[1]

Phosphorus crystallizes with the velocity of 60,000 mm per minute, while salol, one of the substances used in the experiments already referred to, crystallizes at the rate of 4 mm in one minute.

This experiment confirms the conclusion already drawn in the preceding paper, *viz.*—that the crystallization through membranes depends primarily upon the nature of membrane and the dissolved substance.

Supersaturated Aqueous Solutions with Rubber Membranes

In the first paper on this subject, reference was made to some experiments which tended to show that if very thin rubber were substituted for the parchment and collodion membranes, crystallization would be transmitted through it. At that time it was not possible to definitely establish this point, which is obviously of great importance—involving as it does the question of whether actual contact with the solid phase is necessary for the separation of crystals from a supersaturated solution.

A series of very carefully performed experiments was carried out in order to decide this question. The apparatus used is shown in Fig. 2, which is simply a 250 cc distilling

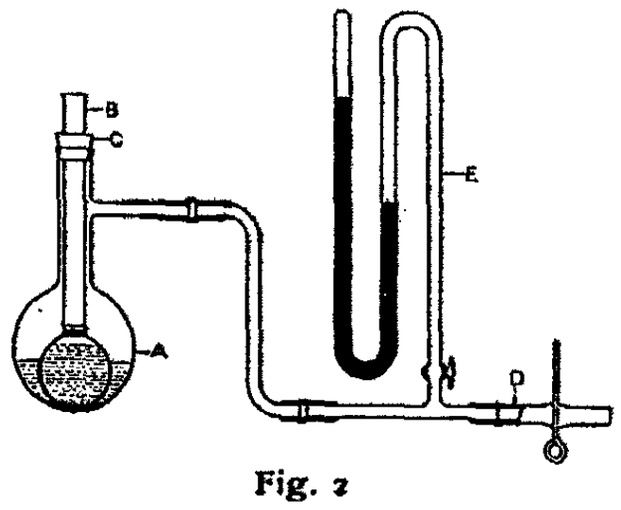

Fig. 2

flask connected with a manometer. About 25 cc of the supersaturated solution was placed in A; it was then boiled for a

[1] Friedländer and G. Tammann: Zeit. phys. Chem., 24, 152 (1897).

few minutes so that the steam would condense on the neck of the flask and wash down any solid particles which might by any chance be lodged there. The stopper C—carrying a glass tube, B over the end of which was tied a piece of sheet rubber, was then inserted in the neck of the flask, and the liquid allowed to cool to the room temperature, about 23°. The system was then connected with the manometer E, and suction applied at D. This caused the rubber on the tube B to become expanded, its thickness being reduced to 0.0003–0.0004 in. The manometer permits the pressure to be regulated, so that the rubber will not be disrupted by too great a pressure. By means of a pinch cock, D was then closed and the apparatus allowed to stand for an hour. Any leaks in the membrane could be detected by the change in the manometer reading during this time. The tube B was then partially filled with a supersaturated solution of the same concentration as that in the flask, and after a few minutes was inoculated.

Experiments were carried out with the following substances:

Experiment 1.—A supersaturated solution of sodium acetate made by heating 300 grams of the pure crystallized salt with 50 cc of water was used, the flask being filled in the manner described. The solution inside the expanded rubber was inoculated. On standing for 1–2 hours no separation of crystals occurred in the flask. Duplicates were carried out in this experiment.

Experiment 2.—An experiment similar to the above was carried out with a supersaturated solution of potassium alum. The solution used was of no definite concentration. In its preparation a sample of alum consisting of crystals about the size of a pea, was used. About 30 grams were placed in the flask, enough distilled water added to just cover them, and the water heated until the crystals were dissolved, forming a solution supersaturated at room temperature. The rest of the experiment was carried out in a manner similar to that just described. In one experiment no change was noticed after two hours, at the end of which time the rubber film

broke. In a duplicate no crystallization was transmitted through the membrane even after twelve hours.

Experiment 3.—A supersaturated solution of lead acetate was prepared by heating 200 grams of the crystals with 75 cc of water. Four experiments were conducted—the details being similar to the experiments just described. After fifteen hours no transmission of crystallization had occurred.

These experiments indicate the necessity of actual contact of the supersaturated solution with the solid phase before crystallization can occur. They show that with these salts whenever crystallization is transmitted through membranes it is brought about by the formation of the solid phase in the pores of the membrane.

Experiments with Solutions Which Were Only Slightly Supersaturated

In all of the experiments made with aqueous supersaturated solution it was found that whenever water could pass through a membrane crystallization could be transmitted through the membrane. As a result of these experiments, therefore, it might seem reasonable to state the above as a generalization. It must be remembered, however, that the experiments referred to were made with solutions which were very strongly supersaturated, and before any such generalization can be made it is necessary to make similar experiments with solutions which are only slightly supersaturated.

To prove this point experiments were carried out as follows:

A saturated solution of a given salt was prepared and kept at 30° C. It could be supersaturated and the degree of supersaturation controlled by either of the following methods:

1. By lowering the temperature of the bath any desired amount.

2. By measuring out a definite quantity of the saturated solution, raising its temperature fifteen or twenty degrees, dissolving a weighed quantity of the salt, and cooling the solution in the bath to 30° again.

Method 2 was used in these experiments. The supersaturated solution was divided by a membrane, one-half was inoculated, and the other half examined from time to time to see whether or not crystals had formed.

The following experiments were made:

A saturated solution of potassium alum was prepared by saturating at 35°, then placing in a bath at 30° and shaking for several hours in contact with the solid phase.

Twenty-five cc portions of the solution were removed by means of a pipette and placed in beakers containing weighed quantities of the alum. These beakers stood in a bath which was kept at a temperature of 45–50° C. After the alum had dissolved portions of the solution were removed and placed in each of the tubes A and B—shown in Fig. 3, which is simply a large test tube closed with a rubber stopper carrying a smaller tube which has its lower end covered with a membrane. When parchment was used as a membrane considerable difficulty was experienced in fastening it over A in such a manner that it would be perfectly tight. This was accomplished by slipping a piece of rubber tubing over the tube, tying the wet parchment over the end in the usual manner, and allowing to dry. A cylinder of glass—C—of diameter large enough to leave a space of about 3 mm between it and the outer wall of A was slipped over the tube. Molten paraffine was poured into this space, and a suction was applied at the upper end of A to draw the paraffine into all the crevices. The portion of parchment at the immediate lower end of A was kept wet in order to prevent its becoming saturated with paraffine, and thus made water-proof. This makes a very tight joint. Instead of paraffine, sealing wax can be used. Collodion membranes can easily be fastened over the end of the tube by means of liquid collodion.

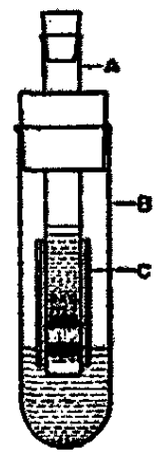

Fig. 3

After introducing the solutions into A and B, they were closed, and shaken so that the hot solution (at 50° C) would dissolve from the stopper or sides of the tube any particles

of the solid phase. The cell was then shaken for 1–2 hours in a thermostat which was kept at a temperature of 30°, to see if spontaneous crystallization would take place. It was then allowed to stand for 2–3 hours and examined for crystals in A or B. If no crystals had separated A was inoculated, and the cell allowed to stay in the bath with frequent shakings, and B examined for crystals from time to time. By holding to the light the separation of even a fraction of a gram of crystalline matter can readily be observed.

The above precautions in filling the cell with warm solution and allowing to stand before inoculating, are absolutely necessary owing to the fact that these supersaturated solutions are so sensitive to the slightest amount of the solid phase. In working in a laboratory in which these substances have been ground, weighed out, etc., it is almost impossible to keep the surfaces of the cell free from the solid phase but by the above precautions these difficulties can be readily controlled.

Experiment 4.—Supersaturated solutions of potassium alum were used with membranes of parchment and inoculated as described above. The degree of supersaturation and the results obtained are recorded in Table 1.

TABLE 1

Results of experiment 4, using supersaturated solutions of potassium alum. Temperature 30° in all cases

Degree of supersaturation[1] Grams	Membrane used	Transmission of crystals through membrane	Length of time in thermostat
1.2	Parchment	No	3 days
2.0	Parchment	No	3 days
4.0	Parchment	No	24 hours
4.0	Parchment	No	4 days
8.0	Parchment	Yes	30 min.
8.0	Parchment	Yes	30 min.
2.0	Collodion	Yes	12 hours
2.0	Collodion	Yes	1 hour

[1] Expressed as grams of substance in 100 cc beyond the amount necessary to saturate the solution at 30°.

It is evident that there is a minimum limit to supersaturation beyond which crystallization is not transmitted through membranes.

With collodion and a supersaturated solution of potassium alum crystallization was transmitted through the membrane. It is of interest to note that with the same concentration, using parchment, no crystals separated in B.

Experiment 5.—Experiments similar to 4 were carried out with solutions of sodium acetate supersaturated to various degrees. The results are shown in Table 2. With parchment, as in the case of the alum solution, there is a minimum limit of supersaturation beyond which crystallization will not pass through the membrane.

TABLE 2

Results of experiment 5, using supersaturated solutions of sodium acetate. Temperature 30° in all cases

Degree of supersaturation[1] Grams	Membrane used	Transmission of crystals through membrane	Length of time in thermostat
1.2	Parchment	No	5 days
2.0	Parchment	No	24 hours
4.0	Parchment	Yes	30 min.
2.0	Collodion	No	3 days
2.0	Collodion	No	7 days
4.0	Collodion	No	7 days
4.0	Collodion	No	7 days

With sodium acetate and collodion membranes it is evident that this limit is higher than with the parchment. That sodium acetate of greater supersaturation does pass through collodion was shown in experiment 3 in the preceding paper.

To be perfectly sure that these collodion membranes which did not transmit crystallization were still permeable to solutions of salts, they were tested with potassium iodide solution. This was found to pass through immediately—a

[1] Expressed as grams of substance in 100 cc beyond the amount necessary to saturate the solution at 30°.

test for the iodide being obtained in the solution on the other side of the membrane. Moreover, in experiments in which crystallization did not pass through—on cooling the liquid in the cell a few degrees, the crystals separated in B at once.

Conclusion

Owing to the complex nature of membranes in general, it is not possible to state the direct cause of this lower limit at which c ystals may be transmitted through membrane.

It seems to the author, however, that the existence of this lower limit points to the fact that the solution within the membrane has a lower concentration than the solution which surrounds the membrane. According to this theory, with a strongly supersaturated solution crystals would be transmitted through the membrane. With a solution whose degree of supersaturation was equal to (or less than) the difference between the concentration of the solution in the membrane and that surrounding the membrane, no transmission of crystallization could occur.

Such a lowering of the concentration of the solution within the membrane could be explained by the formation of a compound of membrane and solute. In the membrane we would have, not only supersaturated solution, but also this compound (membrane + solute) in equilibrium with solution in the pores, and it is easy to conceive of a case in which the solution is supersaturated to such a slight extent that the amount taken up by the membrane leaves in the capillaries of the membrane a solution just saturated or even less than saturated. Such a solution in the membrane would of course not permit the transmission of crystals.

Summary

The results of the foregoing experiments may be summarized as follows:

1. The crystallization of under cooled phosphorus cannot be transmitted through rubber nor gold beater's skin.

2. In the case of supersaturated aqueous solutions the transmission of crystallization through membranes occurs only

in cases in which the membranes are permeable to water. This has been demonstrated by supersaturated solutions of potassium alum, sodium acetate and lead acetate, with rubber membranes 0.0003–0.0004 in. thick. In these cases no transmission took place, even after several hours. Contact with the solid phase is necessary. A new method is described by which rubber membranes of the above thickness may easily be obtained.

3. A minimum limit of supersaturation exists, below which crystallization will no longer be transmitted through membranes which are permeable to water. This phenomenon will be the subject of further investigation.

University of Wisconsin

II. THE SPECIFIC HEAT OF CARBON TETRACHLORIDE AND OF ITS SATURATED VAPOR

BY J. E. MILLS AND DUNCAN MACRAE

The Purity of the Carbon Tetrachloride Used

Some of Baker's "analyzed" C. P. carbon tetrachloride was fractionated over sodium through a Young's fractionating column and considerable trouble was experienced getting a perfectly constant boiling point. So additional commercial carbon tetrachloride was taken and purified as follows:[1] A small stick of potash was dissolved in its own weight of water and added to 200 cc of alcohol. 100 cc of this solution was added to 1000 cc of carbon tetrachloride, the mixture was heated to 50 or 60° C, and shaken for a half hour. The water was poured off and the shaking and heating repeated with 50 cc of alcoholic potash This was repeated a third time. The carbon tetrachloride was then shaken up with 500 cc of water until the mixture rapidly cleared and separated. This was repeated. Water was removed by shaking first with potassium hydroxide and finally with metallic sodium. After standing over sodium for some days the carbon tetrachloride was fractionated until the following pure constant boiling fractions were obtained:

75.90°	under 743.7 mm pressure	= 76.69°	under 760 mm
75.70	under 739.2 mm pressure	= 76.68	under 760 mm
75.99	under 745.9 mm pressure	= 76.66	under 760 mm
75.99	under 746.3 mm pressure	= 76.64	under 760 mm

These fractions amounting in all to about 1000 cc were mixed and constituted the sample tested.

The Method Used

In a former paper[2] the method used was described, the determination of the calorimeter constant was given in detail,

[1] Sammlung chemischer und chemisch-technischer Vorträge, Vol. 10, 1906.

[2] Jour. Phys. Chem., 14, 797 (1910).

and the specific heat of benzol from its freezing point to 70° C was determined. We do not consider it necessary here to repeat any of the explanation there given. The details of the determination of the specific heat of carbon tetrachloride are given below in Table 1. If these details are not immediately understood reference to the former paper will doubtless make them sufficiently clear.

The Results Obtained

The series of experiments 1–5 inclusive, see Table 1, were made with two thermometers that were graduated only to tenths of a degree and were read to hundredths of a degree with a microscope. Experimen s 5–9 were made with a Beckmann thermometer. In experiments 6 and 7 the Beckmann was set at 5.95° and no bath was used. In experiments 8 and 9 the Beckmann was set at 60.02° and the calorimeter was surrounded by a bath held at 59.5°. As related in the previous paper already cited all corrections necessary to reduce the thermometers to the correct hydrogen scale were known. The results are shown plotted in Diagram 1. From the results obtained it appears that the specific heat of carbon tetrachloride from 0–70° C increases only very slightly with the temperature and can be represented by a straight line passing through the values 0.2010 at 0° and 0.2031 at 70° C. The actual values read from this line at intervals of 10° are given in Table 2. We believe that they are correct to one part in 200.

Comparison of the Results with those Obtained by Other Observers

The specific heat of carbon tetrachloride given by other observers[1] is shown in Diagram 1. Calculating the specific heat from the formulae given by Winkelmann for the total heat and the latent heat of vaporization we find the straight

[1] Sammlung chemischer und chemisch-technischer Vorträge, Vol. 10, 1906. Hirn: Ann. chim. phys., [4] 10, 63 and 91 (1867). Winkelmann: Ann. der Physik., 9, 208, 358 (1880). Sutherland: Phil. Mag., [5] 26, 298 (1888). Regnault: Mém. de l'Acad., 26, 761 (1862).

TABLE 1

The specific heat of carbon tetrachloride

Number of experiment	1	2	3	4	5	6	7	8	9
Volts	3.8236	3.9371	4.0236	4.1328	4.2329	2.4887	2.4861	2.8265	2.8274
Amperes	2.9985	2.9985	2.9985	2.9984	2.9984	1.9952	1.9952	1.9946	1.9946
Time in minutes	10	10	10	10	10	10	10	12	13
Total calories added	1642.7	1691.5	1728.7	1775.5	1818.5	711.47	710.76	969.33	1050.44
Correction for vaporization	0.8	1.1	1.5	2.2	2.7	0.30	0.30	1.92	2.05
Temperature before	9.011	19.787	27.860	38.453	47.797	1.071	0.907	−0.105	−0.044
Temperature after	19.524	30.535	38.790	49.611	59.072	5.560	5.431	5.933	6.443
Δt	10.513	10.748	10.930	11.158	11.275	4.489	4.524	6.038	6.487
Average temperature	14.27	25.16	33.32	44.03	53.43	9.27	9.12	62.93	63.22
Calories added per degree	156.18	157.28	158.02	158.93	161.05	158.44	157.04	160.22	161.61
Calorimeter constant	12.95	13.78	14.40	15.20	16.03	14.65	14.65	17.25	17.25
Weight of CCl_4	711.12	711.12	711.12	711.12	711.12	714.11	712.75	712.24	714.35
Specific heat of CCl_4	0.2014	0.2018	0.2020	0.2021	0.2039	0.2014	0.1998	0.2007	0.2021

line shown in the diagram. Regnault determined the total heat of carbon tetrachloride to 160°, finding at 160° the value 71.00 calories, in good agreement with the value, 71.21 calories, obtained by Winkelmann. Using the value obtained by Regnault and the value of the heat of vaporization at this temperature, 37.95 calories,[1] we find that the average specific heat of carbon tetrachloride from 0–160° is 0.2066 calories.

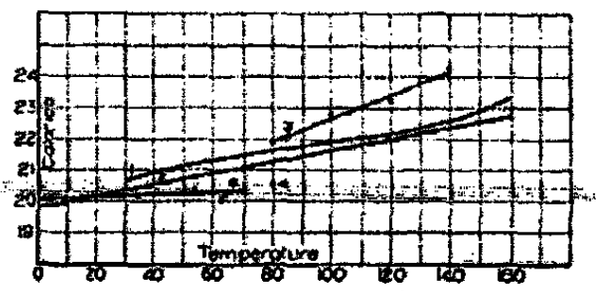

Fig. 1

1. Hirn.
2. Winkelmann.
3. Sutherland.
4. From Regnault.
5. Mills and MacRae.

This average value is probably nearly correct though it is somewhat higher than the probable true value at 80° C. The values obtained by the authors for the specific heat of carbon tetrachloride are shown in the diagram and indicate that at low temperatures the specific heat of carbon tetrachloride does not increase so rapidly with the temperature as has been supposed.

The Specific Heat of the Saturated Vapor

If the heat of vaporization of the liquid at intervals of 10° and the specific heat of the liquid are known, the specific heat of the saturated vapor may be calculated. For the energy necessary to change the liquid at 0° into the saturated vapor at 10° is the same whatever may be the method pursued to effect the change. Letting the subscripts of L denote temperature, and letting σ_L denote the total heat added to the

[1] Sci. Proc. Roy. Dublin Soc., 12, 427 (1910).

liquid and σ_v that added to the vapor between the temperature limits given, we have,

1. $$L_0 + \sigma_v = L_{10} + \sigma_L, \text{ or } \sigma_v = L_{10} + \sigma_L - L_0.$$

By this method we have calculated the values for the specific heat of the saturated vapor at intervals of 10° from 5–65° from the data given in Table 2 and give the results in that table.

The heats of vaporization marked "Ther" were calculated by use of the thermodynamical equation,

2. $$L = 0.0_43183 \frac{dP}{dT} T(V - v) \text{ calories,}$$

from the data[1] given in Table 2. In this equation L is the heat of vaporization, T is absolute temperature, P is pressure in millimeters of mercury, and v and V are the volumes of a gram of the liquid and of its saturated vapor.

The values of the heat of vaporization in the column marked "Mills" are obtained by using the equation,

3. $$L = \mu'(\sqrt[4]{d} - \sqrt[4]{D}) + E_s.$$

Here μ' is a constant for any particular substance and for carbon tetrachloride has the value 44.01. E_s is the energy expended in overcoming the external pressure as the liquid expands to the volume of the saturated vapor and is given by the equation,

4. $$E_s = 0.0_43183\, P(V - v) \text{ calories.}$$

Equation 3 has been carefully and extensively studied[2] and seems to hold accurately for non-associated liquids at all temperatures.

[1] See Sci. Proc. Roy. Dublin Soc., 12, 427 (1910), except the density and volume of the saturated vapor from 0–60° inclusive. At 0° the values are the theoretical values. At 10–60° they are obtained by extrapolating an equation given by Young: Journal de Physique, Jan., 1909.

[2] See particularly Jour. Phys. Chem., 13, 512 (1909), and Jour. Am. Chem. Soc., 31, 1099 (1909), and references there given.

TABLE 2

The specific heat of the saturated vapor of carbon tetrachloride

Temperature	Vapor pressure P	Density of liquid d	Volume of liquid v	Density of vapor D	Volume of vapor V	External energy E_E	$\sqrt[3]{d}$	$\sqrt[3]{D}$	$\sqrt[3]{d} - \sqrt[3]{D}$
0° C	33.08	1.6327	0.6125	0.0_32984	3351	3.52	1.1775	0.06683	1.1107
10	35.51	1.6132	0.6199	0.0_34879	2050	3.62	1.1728	0.07873	1.0941
20	89.61	1.5939	0.6274	0.0_37614	1313	3.74	1.1681	0.09132	1.0768
30	139.64	1.5748	0.6350	0.001150	869.6	3.86	1.1634	0.10476	1.0586
40	210.71	1.5557	0.6428	0.001686	593.3	3.98	1.1587	0.11901	1.0397
50	308.09	1.5361	0.6510	0.002399	416.7	4.08	1.1538	0.13389	1.0199
60	440.67	1.5165	0.6594	0.003347	298.8	4.18	1.1489	0.14958	0.9993
70	613.8	1.4963	0.6683	0.004570	218.8	4.26	1.1438	0.16595	0.9779

TABLE 2—(*Continued*)

Temperature	Specific heat of liquid	Heat of vaporization		Specific heat smoothed		Specific heat unsmoothed			
		Ther.	Mills	Ther.	Mills	Temp.	Ther.	Mills	
0° C	0.2010	51.83	52.40	0.170	0.140	5	0.1172	0.138	—
10	0.2013	50.99	51.77	0.160	0.138	15	0.1535	0.137	—
20	0.2016	50.51	51.13	0.150	0.135	25	0.1478	0.134	—
30	0.2019	49.97	50.45	0.140	0.132	35	0.1371	0.131	—
40	0.2022	49.32	49.74	0.130	0.128	45	0.1254	0.125	—
50	0.2025	48.55	48.97	0.120	0.124	55	0.1247	0.122	—
60	0.2028	47.77	48.16	0.110	0.119	65	0.1040	0.117	—
70	0.2031	46.78	47.30	0.100	0.115	—	—	—	—

While equation 2 is correct if the data is absolutely accurate we have shown in the paper cited that slight inaccuracies in the data are often greatly multiplied in their proportionate effect upon the values of the heat of vaporization. For this reason we consider the smoothed values of the specific heat of the saturated vapor as given under the heading "Mills" in Table 2 to be the most accurate.

Analysis of the Specific Heat of Benzol and of Carbon Tetrachloride

The object of this research was to throw light upon the nature and cause of the energy changes involved during the rise in temperature of a liquid. So far as the writers are aware the specific heat of any substance is supposed to be due to the following energy changes:

1. *The energy necessary to overcome the external pressure as the substance expands.*—This energy can be easily calculated if the external pressure and the volumes before (v) and after (v') expansion are known. If the pressure is given in millimeters of mercury and the volumes of a gram in cubic centimeters, the equation takes the form,

5. $$E_{External} = E_e = 0.0_4 3183\ P(v' - v) \text{ calories.}$$

2. *The energy necessary to overcome the molecular attraction as the substance expands.*—The investigation upon molecular attraction by one of the authors[1] has led to the belief that this amount of energy can be calculated from the equation,

6 $$E_{attraction} = E_a = \mu' (\sqrt[3]{d} - \sqrt{d'}),$$

where μ' is a constant characteristic of the substance, and d is the density of the substance before, and d' the density of the substance after, expansion. This equation is certainly applicable to the expansion of a liquid at constant temperature and under constant pressure from its volume as a liquid to its volume as a saturated vapor. That it is likewise ap-

[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383 (1904); 8, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132 (1907); 11, 594 (1907); 13, 512 (1909); Jour. Am. Chem. Soc., 31, 1099 (1909).

plicable to the expansion of a substance when both temperature and pressure are variable has not been proved, but it seems to the authors likely to constitute at least one *term* of the energy necessary for such expansion. We expect the investigation when completed to throw light upon this point.

3. *The energy necessary to increase the translational motion of the molecules as the temperature of the substance is raised.*—If the substance is a perfect gas and the kinetic theory of gases is true, the total amount of this translational energy for 1 gram of substance is, at the absolute temperature T, simply $\frac{2.982\,T}{m}$ calories. Therefore,

$$7. \qquad E_{\text{kinetic}} = E_k = \frac{2.982}{m} \text{ calories,}$$

where m is the molecular weight of the substance. It is possible that equation 7 does not apply to substances whose molecules are under the action of attractive forces, more particularly solids and liquids. To obtain further evidence upon this point was one of the objects in view in the present investigation.

4. *An amount of energy which we propose to call "internal energy", the office of the energy being unknown.*—This energy is roughly proportional to the number of atoms within the molecule, being zero for a monatomic molecule, such as mercury or argon. If from the specific heat of the substance as a perfect gas at constant volume, the kinetic energy necessary to raise the temperature of the substance 1° (see 3 above) be subtracted, the remainder is the internal energy as we have defined it. This "internal energy" change is probably not a change of the chemical energy of the atoms within the molecule, but seems to be required for even the most stable polyatomic molecule. It may have to do with the rotation of the molecule as a whole. Numerous attempts, of which particularly the efforts of Boltzmann may be mentioned, to give a satisfactory explanation of this internal energy have failed. For a perfect gas, while the gas is chemically stable, the

internal energy appears to be proportional to the translational energy and may be obtained from the equation,

$$8. \qquad E_{\text{Internal}} = E_t = \frac{5/3 - \gamma}{\gamma - 1} E_k,$$

where γ is the ratio of the specific heat of the gas at constant pressure to its specific heat at constant volume.

5. *The energy which binds the atoms together.*—This energy might be called chemical energy. We are inclined to believe that for a stable chemical compound, far removed from its point of decomposition, the chemical energy of the body is not affected by changes in temperature.[1]

Hence except for a substance nearing the point of, or undergoing, decomposition, we think that,

$$9. \qquad E_{\text{chemical}} = E_c = 0.$$

6. *Other possible energy changes.*—It is well to bear in mind that there may be other energy changes of which we know nothing. Thus the total heat added to a solid, probably monatomic, metal to raise its temperature from —273° C to its melting point and bring it into the liquid condition is about $9T/m$ calories. This amount of energy is far greater than has yet been accounted for. Therefore for the present we have called,

$$10. \qquad E_{\text{unknown}} = E_u = \sigma - (E_e + E_a + E_k).$$

Whether E_u will prove identical with E_t is a very interesting point.

We have in the manner indicated analyzed the specific heat of benzol and of carbon tetrachloride and give the results in Tables 3 and 4. The data for benzol is given in the former paper already cited. The measurements have not yet been carried over a sufficient range of temperature, nor extended to enough substances, to enable conclusions to be drawn with certainty. We would, however, call attention to the following points:

[1] Trans. Am. Electrochem. Soc., 14, 35 (1908).

TABLE 3

Analysis of the specific heat of benzol

Temperature	Specific heat of liquid					Specific heat of saturated vapor				
	σ_{liquid}	E_e	E_a	E_k	E_u	σ_{vapor}	E_e	E_a	E_k	E_u
0° C	0.3970	Not appreciable	0.0413	0.0382	0.3175	0.284	0.025	0.0975	0.0382	0.318
10	0.4027		0.0415	0.0382	0.3230	0.282	0.025	0.1040	0.0382	0.323
20	0.4084		0.0420	0.0382	0.3282	0.279	0.024	0.1108	0.0382	0.328
30	0.4141		0.0424	0.0382	0.3335	0.277	0.024	0.1174	0.0382	0.332
40	0.4198		0.0431	0.0382	0.3385	0.275	0.023	0.1240	0.0382	0.338
50	0.4255		0.0437	0.0382	0.3436	0.273	0.022	0.1308	0.0382	0.344
60	0.4312		0.0448	0.0382	0.3482	0.270	0.020	0.1373	0.0382	0.349
70	0.4369		0.0459	0.0382	0.3528	0.268	0.018	0.1438	0.0382	0.356

$m = 78.05$ $\mu' = 109.26$. The results under E_a and E_e were smoothed

TABLE 4

Analysis of the specific heat of carbon tetrachloride

Temperature	Specific heat of liquid					Specific heat of saturated vapor				
	σ_{liquid}	E_c	E_a	E_k	E_u	σ_{vapor}	E_c	E_a	E_k	E_u
0° C	0.2010	Not appreciable	0.0207	0.0194	0.1609	0.140	0.0115	—0.0506	0.0194	0.160
10	0.2013		0.0207	0.0194	0.1612	0.138	0.0115	—0.0538	0.0194	0.161
20	0.2016		0.0207	0.0194	0.1615	0.135	0.0115	—0.0573	0.0194	0.161
30	0.2019		0.0209	0.0194	0.1616	0.132	0.0115	—0.0607	0.0194	0.162
40	0.2022		0.0211	0.0194	0.1617	0.128	0.0110	—0.0641	0.0194	0.162
50	0.2025		0.0216	0.0194	0.1615	0.124	0.0100	—0.0674	0.0194	0.162
60	0.2028		0.0220	0.0194	0.1614	0.119	0.0090	—0.0706	0.0194	0.161
70	0.2031		0.0224	0.0194	0.1613	0.115	0.0080	—0.0735	0.0194	0.161

$m = 153.8$ $\mu' = 44.01$. The results under E_a and E_c were smoothed

(*a*) The energy changes in the saturated vapor due to the molecular attraction are far greater than has usually been supposed.

(*b*) The total energy change unaccounted for, which we have called the unknown energy, and designated E_u, is a constant for carbon tetrachloride to within the limit of error of the measurements. It is not a constant for benzol.

(*c*) If we compare the energy changes at 0° C of molecules of benzol and carbon tetrachloride we find them similar to a remarkable degree as shown below.

LIQUID.

	$\sigma \times m$	$E_k \times m$	$E_a \times m$	$E_u \times m$
Benzol	30.98	2.98	3.22	24.78
Carbon tetrachloride	30.91	2.98	3.18	24.74

SATURATED VAPOR.

	$\sigma \times m$	$E_e \times m$	$E_a \times m$	$E_u \times m$
Benzol	22.17	1.95	—7.61	24.84
Carbon tetrachloride	21.53	1.77	—7.78	24.55

(*d*) γ has been measured for benzol by Stevens[1] who obtained the value 1.105 at 99.7°, and by Wiedemann[2] who obtained the value 1.129. For carbon tetrachloride Capstick[3] obtained the value 1.130. For benzol using the value of Stevens we obtain 0.2044 for E_i from equation 8. For carbon tetrachloride similarly we obtain 0.0800. When γ is nearly equal to one slight errors in the measurement of γ cause greatly increased errors in E_i and it is unfortunate that for this reason no very great reliance can be placed upon these values.

(*e*) The total heat necessary to raise 6.05 grams of hydrogen from —273° to 20° C is 6740 calories.[4] The total heat

[1] Stevens: Ann. der Physik., [4] 7, 285 (1902).
[2] Wiedemann: Wied. Ann., 2, 195 (1877).
[3] Capstick: Proc. Roy. Soc., 57, 322 (1895).
[4] Trans. Am. Electrochem. Soc., 14, 35 (1908).

necessary to raise 72 grams of carbon as graphite from —273° to 20° is approximately 1480 calories, and similarly as diamond 800 calories.[1] Nordmeyer and Bernouilli[2] have determined the average specific heat of benzol from 20° to —185° C to be 0.176, allowing 30 calories for the heat of fusion. Estimating the average specific heat of benzol from —185° to —273° to be 0.08 we find that 5707 calories of energy would be required to raise the temperature of 78.05 grams of benzol from —273° to 20° C. If the carbon and hydrogen existed as elements the necessary energy for a similar rise in temperature would be 7540 calories if the carbon were in the form of diamond, and 8220 calories if the carbon were in the form of graphite. Since about 1745 calories of this energy is due to external work this amount might be subtracted, leaving 5795 and 6475 calories respectively. Nearly as much energy is therefore required to raise the temperature of the carbon and hydrogen from —273° to 20° C when they are combined to form benzol as when they exist separately.

Summary

1. The specific heat of liquid carbon tetrachloride is found to vary linearly with the temperature between 0° and 70° C. The line passes through the values 0.2010 at 0° and 0.2031 at 70° C.

2. The specific heat of the saturated vapor of carbon tetrachloride has been determined and the following values obtained, 0° = 0.140, 10° = 0.138, 20° = 0.135, 30° = 0.132, 40° = 0.128, 50° = 0.124, 60° = 0.119, 70° = 0.115.

3. The results obtained both for carbon tetrachloride and for benzol have been discussed and certain facts concerning the energy changes involved have been pointed out.

The above work was done in the chemical laboratory of the University of North Carolina.

University of North Carolina,
August 11, 1910

[1] Dewar: Proc. Roy. Soc., 76*a*, 325 (1905).
[2] Verh. der deutsch. Phys. Ges., 9, 175 (1907).

THE SOLUBILITY OF LIME IN AQUEOUS SOLUTIONS OF SUGAR AND OF GLYCEROL[1]

BY F. K. CAMERON AND H. E. PATTEN

Introduction

In a previous publication from this laboratory[2] a résumé was given of the extant data upon the solubility of lime in various solutions. It was concluded that when lime is brought into contact with sugar solutions, the ratio of lime to sugar in the solid varies continuously with the composition of the solution; and consequently the solid compound resulting when lime is added in excess to a sugar solution is one of a series of solid solutions. The data on record, however, possess the common defect that the quantities of sugar remaining in solution after contact with the lime were not determined. The original sugar concentrations of the solution were known, and the quantities of lime dissolved by it were determined; but the sugar in the resulting solution not being determined, there is a possibility that some of the sugar may have been precipitated in the solid (lime) phase. While the existence of a compound of lime with sugar is known, and this fact would indicate the strong probability that some sugar at least would be withdrawn from a sugar solution in contact with excess of lime, yet it is to be remembered that water breaks down the crystalline lime-sugar compound.

The System, Lime-Sugar-Water at 25°

Cane sugar solutions varying from 0.5–40 percent were prepared, and slaked lime added to each in slight excess. The physical properties of the system, lime-sugar-water, are such as to render difficult the attainment of equilibrium conditions. The lime compacts into balls and cakes and these

[1] Published by permission of the Secretary of Agriculture.

[2] The action of water and aqueous solutions upon soil carbonates. F. K. Cameron and J. M. Bell, Bull. No. 49, Bureau of Soils, U. S. Dept. of Agriculture (1907).

resist disintegration into a flocculent sediment, even under months of shaking in a thermostat. Consequently to ensure the formation of a solid phase in final equilibrium with the solution, it was found desirable to saturate the sugar solution with lime at a low temperature—about 0° C—where it is more soluble, and then pour off the supernatant solution. This saturated liquid was then allowed to warm up to 25° with constant agitation in the thermostat. The solid phase which deposited from solution was finely d vided and showed no tendency to form aggregates.

The sugar solutions are of course very viscous at room temperature. The viscosity decreases rapidly with rise in temperature, but the solubility of lime in these solutions also decreases. If the stiff solution be heated in order to stir it, then fine particles of solid phase appear throughout the liquid, and if these be allowed to settle while the solution is hot, then on cooling, the supernatant liquid—which has again become stiff—regains its higher solvent power for lime. It is well nigh impossible to bring this stiff liquid into intimate contact with a sufficient surface of solid phase to ensure equilibrium. Consequently it was found impracticable to study the lime-water-sugar system at high concentrations of sugar and lime. The fact that considerable lime will dissolve in these stiff syrups may of course be shown and is of interest in itself, but the main object of the present work is to determine the character of the solid phase under equilibrium conditions, and the stiffer sugar solutions are not adapted to this purpose.

The complete dry combustion of the solution was made in oxygen supplemented by copper oxide, the carbon of the sugar being weighed as carbon dioxide; and the solvent wate plus the constitutional water of the sugar were weighed together as water. Given the weight of carbon dioxide, the weight of constitutional water in the sugar can be computed, and deducting this leaves the water originally added to make up the solution. The lime in solution was determined separately by evaporating the solution in platinum, burning off the sugar

and igniting before the blast lamp. In the case of a solid phase rich in lime, the combustion was carried out at high temperature to decompose the calcium carbonate formed. Several combustions at lower temperature left a residue in the combustion boat rich in carbonate, but by using a higher temperature, not a trace of carbonate remained. For the solid phase the percentage of lime is so high and the carbon dioxide and water determinations so accurate, that the lime was in some cases taken by difference; but the solutions were analyzed for lime directly in every case.

The solid phase obtained was in no case crystalline. Under the microscope it appeared as fine globular granules. consequently a sharp separation from the mother liquor was not feasible. To obviate this difficulty the solutions were allowed to settle in the thermostat for several weeks, and the clear liquid phase poured off from the pasty sediment. This residual lime-paste was scraped into a glass-stoppered weighing bottle, placed in a padded glass test tube and centrifuged at about 800 r. p. m. for two or three days until the solid showed no further signs of settling. The supernatant liquid was poured out of the bottle and the last few drops absorbed with clean filter paper. The weighing bottle was then weighed, the solid phase scooped out with a small platinum spoon and removed to a long combustion boat by means of a platinum scraper. Both spoon and scraper were placed in the combustion boat which was immediately transferred to the combustion tube in place in the furnace. The closely stoppered weighing bottle was again weighed and the difference from the former weight gave the weight of the solid phase and mother liquor taken for analysis.

The compositions of the solutions are given in Table I. The lime present is reckoned as $Ca(OH)_2$ for convenience, especially as it was anticipated that the solid phase might prove to be calcium hydroxide. On the other hand, there is no particular advantage in stating the results as calcium oxide. In Fig. 1 the calcium hydroxide in solution is plotted as a function of the sugar. The curve thus obtained is smooth,

TABLE I

Lime-sugar-water system at 25° C. Liquid phase.

$Ca(OH)_2$ percent	$C_{12}H_{22}O_{11}$ percent	H_2O percent	Density
0.117[1]	0	—	0.983
0.188	0.62	99.19	1.000
0.73	4.82	94.50	1.021
1.355	7.50	91.12	1.037
2.31	9.87	87.85	1.051
3.21	11.90	84.89	1.067
4.57	15.1	80.33	1.092
5.38	17.42	76.93	1.109
6.07	19.86	73.07	1.123

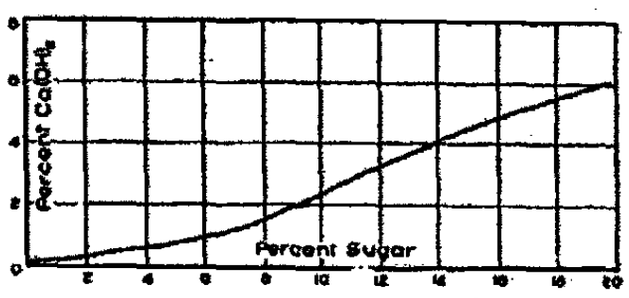

Fig. 1

showing no obvious breaks, and passing of course through the point for the solubility of calcium hydroxide in water alone. Consequently the solid phases in contact with the solutions represented by this isotherm must be either calcium hydroxide, or a series of solid solutions with calcium hydroxide, as a limiting solid solution at one end of the series.

Attempts were made to determine the nature of the solid phases by the indirect method of Schreinemakers[2] and Bancroft,[3] employing the triangular diagram, but owing to the viscosity of the solutions, satisfactory separations of solid from mother liquor could not be obtained even under long centrifuging. Consequently the results were indeterminate and the method was abandoned.

A solution was prepared containing 303.24 grams of water,

[1] Cameron and Bell, l. c.
[2] Zeit. phys. Chem., 11, 81 (1893).
[3] Jour. Phys. Chem., 6, 178 (1902).

and 100 grams of sugar. To this solution was added 63.88 grams of calcium hydroxide. After long standing with intermittent shakings at 25° C analysis of the supernatant solution gave 21.97 percent sugar, 8.32 percent calcium hydroxide and 69.71 percent water (by difference). The ratio of water to sugar in the liquid phase was therefore increased by the addition of lime from 3.03–3.17, showing that sugar entered the solid phase. Consequently the solid phases were a series of solid solutions. That the absorption of sugar in the solid phase may be considerable is shown by the fact that in this particular case just cited the solid contains about 10.8 percent sugar, assuming that the ratio of lime to water remains that in calcium hydroxide.

The System, Lime-Glycerol-Water at 25°

This system presents experimental difficulties similar to the one just described owing to the great viscosity of the more concentrated solutions. The solubility data are given in Table II. When plotted they give a straight line passing through the point representing the solubility of calcium hydroxide in water.

TABLE II

Lime-glycerol-water system at 25° C. Liquid phase

Experiment number	$Ca(OH)_2$ percent	$C_3H_5(OH)_3$ percent	H_2O percent	Density
O	0.117	0	—	—
α	0.178	3.50	96.32	1.008
β	0.413	15.59	80.28	—
A	0.48	17.84	81.68	1.042
B	0.88	34.32	64.80	1.088
C	1.34	55.04	43.62	1.149

A solution was prepared containing 35.9 percent glycerol, to which was added about 40 grams calcium hydroxide. This system was agitated for several hours in an ice bath, then allowed to come gradually to 25°. Analysis of the supernatant solution gave 36.2 percent glycerol and 0.93 percent

lime. Evidently no glycerol entered the solid phase, and the slight apparent increase in the liquid phase can most probably be attributed to the difficulties of analysis. It is apparent that the solid phase in contact with a water glycerol solution at 25° is always calcium hydroxide. Furthermore, the solubility of calcium hydroxide is increased proportionally to the concentration of glycerol.

Summary

(1) Solubility isotherms for lime in solutions of sugar and of glycerol at 25° have been determined by direct analysis of the liquid phases.

(2) The solid phase in the system lime-sugar-water is one of a series of solid solutions, with calcium hydroxide a limiting case.

(3) The solid phase in the system lime-glycerol-water at 25° is always calcium hydroxide.

(4) The increase in solubility of lime in aqueous solutions of glycerol over that in pure water is directly proportional to the concentration of glycerol.

Bureau of Soils,
U. S. Department of Agriculture,
Oct. 5, 1910

THE USE OF A DEWAR FLASK IN MEASUREMENTS OF HEATS OF NEUTRALIZATION

BY J. HOWARD MATHEWS AND A. F. O. GERMANN

Many attempts have been made to devise a simple laboratory method for the accurate determination of heats of neutralization. The method in most common use is cumbersome, and has some other very serious objections. The chief of these is the necessity of removing one of the reacting liquids from its calorimeter and pouring into the other; an operation which introduces a temperature change the magnitude of which cannot be estimated, and for which consequently no correction can be applied. Of importance also is the fact that two thermometers are required, which may introduce considerable error if they have not been accurately compared and standardized against each other.

To overcome these objections various devices have been tried. Thus Julius Thomsen placed one calorimeter above the other and mixed the liquids after temperature equilibrium had been reached, by allowing the upper liquid to flow into the lower. Nernst tried to remove the necessity of the second thermometer and at the same time insure temperature equilibrium before mixing by immersing the acid, contained in a large test tube, in the alkali, and breaking the tube when temperature equilibrium had been reached. Kahlenberg has used a somewhat similar device in that he replaced the test tube by a thin glass flask open at both ends, over the bottom of which he placed paraffined paper. The latter could be broken without difficulty and was easily replaced. Rubber membranes have also been used. Still others have used a collapsible cup for holding one of the reacting liquids until temperature equilibrium was attained.

In both the Thomsen and Berthelot methods, and their various modifications, the correction for radiation is often large and necessarily of somewhat uncertain value. Furthermore, heat radiation is undesirable because it also accentuates

the error due to thermometric lag.[1] The adiabatic method devised by Richards and Rowe,[2] is of course, the best method so far devised for the determination of heats of neutralization where very accurate results are required.

The primary object of the present investigation was to devise an apparatus of simple construction which would be free from the more prominent sources of error in the Berthelot and Thomsen methods. Preliminary experiments in which two Dewar cylinders replaced the customary calorimeter and concentric polished cylinders of the Thomsen method or the calorimeter and surrounding water jacket of the Berthelot method showed a very great improvement, as the radiation correction became very small because of the superior insulation afforded by the Dewar flasks. This makes the radiation correction more certain in value and reduces the error due to thermometric lag, although it does not entirely eliminate it.

We then conceived the idea of replacing the large and cumbersome calorimeter in common use by a Dewar flask, and of using a cylindrical tube of thin glass whose lower end was closed by a rubber septum to separate the acid from the base; and, further, of determining the heats of neutralization of several acids with sodium hydroxide at different concentrations to ascertain the general applicability of the method.

A silvered Dewar flask (see figure) of about 600 cc capacity constitutes the calorimeter. The glass cell B has a capacity of about 250 cc, and fits loosely into the flask. At the bottom is a flange over which a small piece of dentist's rubber dam may be tightly drawn, and held by a rubber band. The cell B is attached to a brass sleeve and eccentric, which gives it a vertical motion, guided by a central modified Witt stirring rod C, whose motion is rotary. By th's means the two solutions, both within and without the cell B, are well stirred. The flask is closed by a cork stopper containing two holes; one in the center to allow the passage of the central stirring

[1] Richardson, Henderson and Forbes: Proc. Am. Acad., 41, 1; Zeit. phys. Chem., 52, 551 (1905).

[2] Zeit. phys. Chem., 64, 187 (1908).

rod and the pitman attached to the crank, and the other at one side for the entrance of the thermometer. The latter dips into the liquid contained in the cel B. The cork is covered with bright tinfoil to reduce radiation.

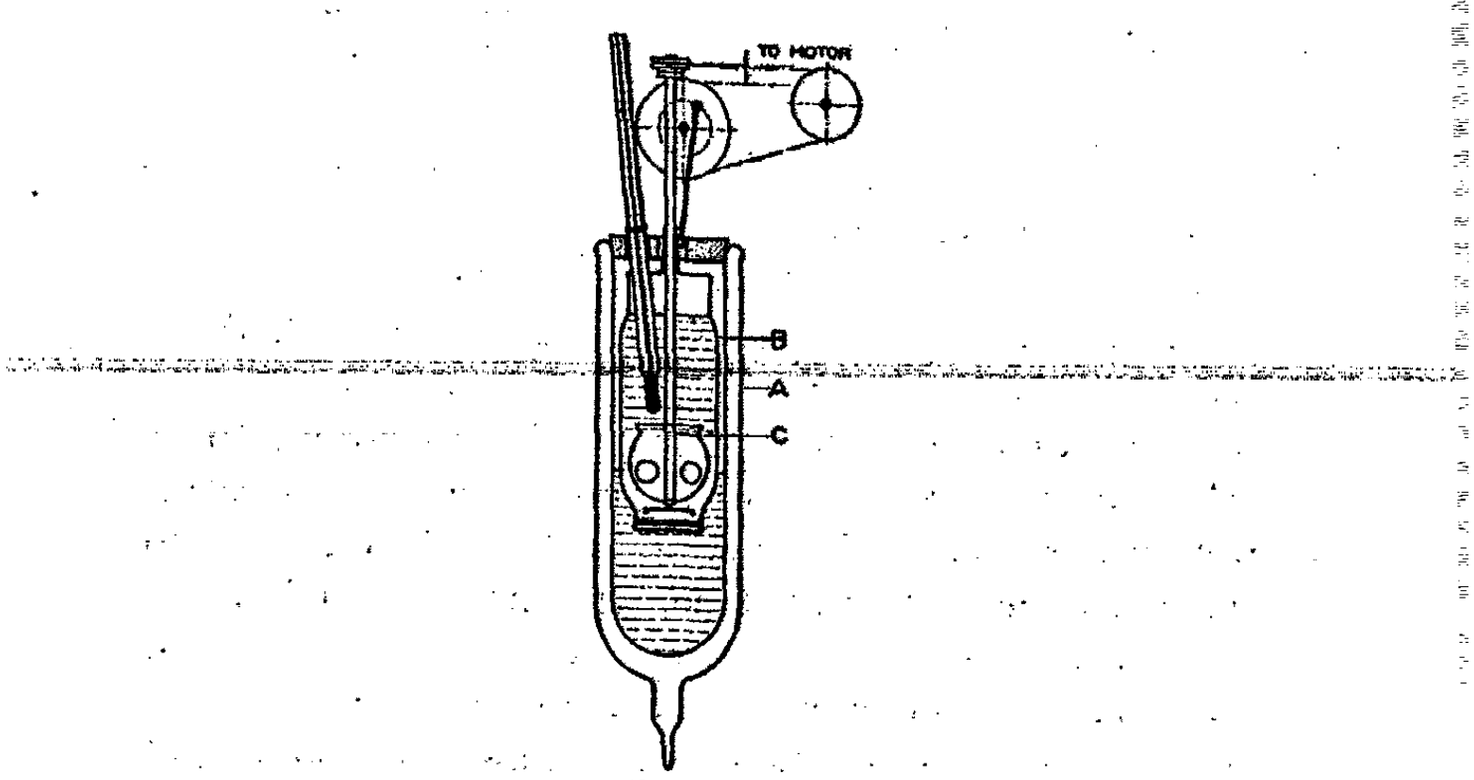

Fig. 1

The thermometers used were a Beckmann and two others not of the differential type. One of the latter was graduated to twentieths of a degree, and read from 15°–30°; and the other read from 18°–25° and was graduated to hundredths of a degree, as was also the Beckmann. The instruments were all of Goetze's make and of the best grade. They were not standardized for this work, however, since we had in mind only the testing out of the method to ascertain its adaptability to general laboratory practice. Therefore the values here given are in no wise to be interpreted as a revision of Thomsen's values. Nevertheless we believe that we have demonstrated that by the method here described a high degree of accuracy may be attained.

The acid solutions were made up in carbon dioxide free water, and were carefully checked against each other. Half normal hydrochloric acid, standardized gravimetrically by precipitation as silver chloride, was used as the starting point.

The sodium hydroxide was Merck's "from alcohol," and was freed from carbonate by making up first a 1 : 1 solution, in which sodium carbonate is very insoluble, filtering, and making up to the required strength. For the half normal solutions sodium hydroxide prepared from metallic sodium, by allowing to stand in a platinum dish over water in a desiccator protected with a soda-lime tube, was also used. The thermal data obtained by the use of the solutions prepared in these two ways checked so closely that the Merck product, purified as described, was used for the other concentrations.

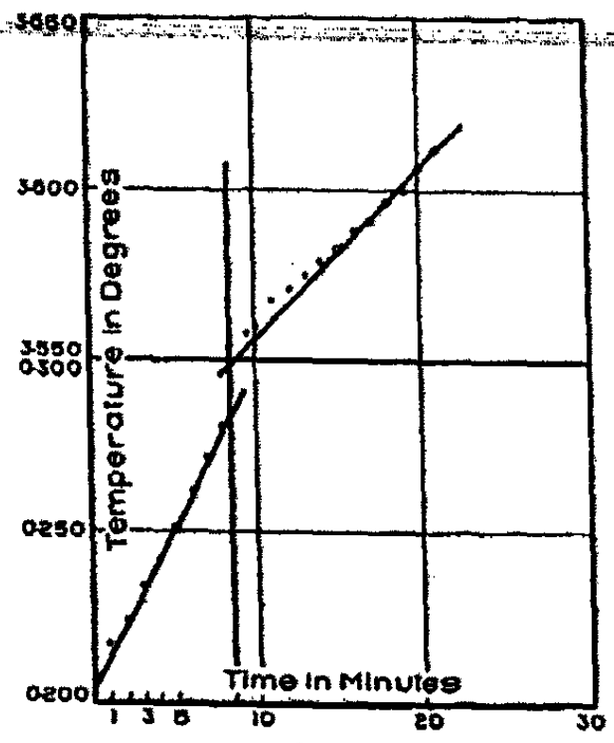

Fig. 2
(Curve I)

The initial temperature of the determinations for all but the twice normal solutions was 18°. For twice normal sulphuric acid the initial temperature was about 15°, and for the other twice normal solutions about 16°. The solutions after being brought to the desired temperature were measured from a 200 cc pipette, the exact capacity of which had been determined, and the excess of the acid or alkali was ascertained after each experiment by titration, using phenolphthalein as an indicator. The motor was run at such a rate that the cell B plunged up and down about once per second; while the

central stirring rod was geared so as to make about four or five revolutions per second. The initial temperature of the base, which was always placed in the cell B, was always a little higher than that of the acid. This gave an opportunity to determine when temperature equilibrium was established, for the thermometer, which was placed in B, at first showed a slow drop in temperature, came to a minimum, and then finally began to rise again due to communication of heat from without the apparatus. The minimum reading showed temperature equilibrium, and this was always reached in less than

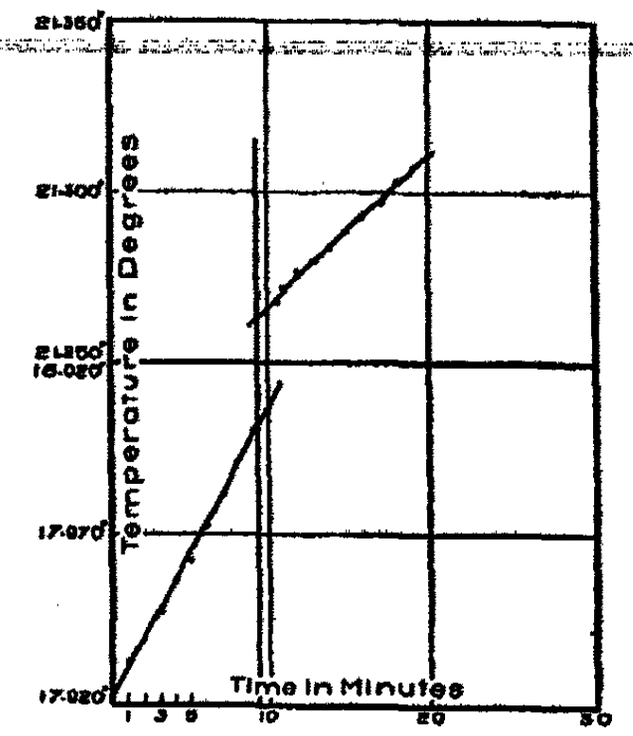

Fig. 3
(Curve II)

five minutes. Temperature readings were made at intervals of one minute. When the thermometer seemed to be rising regularly the stirring rod, which was provided with two sharp copper points at the base, was lowered without interrupting the stirring, so that the points, coming in contact with the tightly stretched membrane, tore the latter and allowed the solutions to mix. At the same time the flask was raised, thus plunging the cell with its contents into it to such a depth that the solution could flow over the top of the cell B and thus insure thorough mixing in the least possible

time. The time at which the mercury thread of the thermometer began to rise was noted and taken as the time of mixing. One minute was required for the thermometer to register the total rise in the case of the normal, half normal and twice normal solutions; thirty seconds for the quarter normal. The temperatures were plotted against the time, and by a slight extrapolation the exact temperature of the solution before and after mixing was found. It was found that about five minutes were necessary for the glass flask, etc., to assume the temperature of the solution; hence only those temperatures should be considered which were taken after the expiration of this time, *i. e.*, the time required for temperature equilibrium.

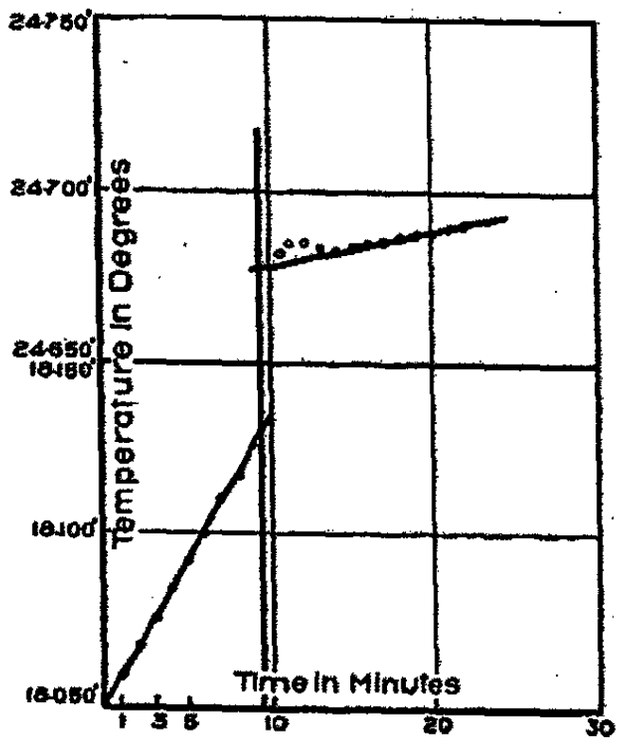

Fig. 4
(Curve III)

The water equivalent of the apparatus could not be determined directly, but was found indirectly by allowing a reaction of known thermal value to take place in it, and from this calculating the water equivalent. The reaction employed was the neutralization of half normal hydrochloric acid by sodium hydroxide. The heat of neutralization is given by Julius Thomsen in this case as 13,740 calories at

18°. The mean of two concordant determinations was taken as the true value, and was found to be 23.2 grams. The data and computations appear in the following table:

I. To Determine the Heat Capacity of the Apparatus, as Expressed in Terms of the Water Equivalent

Volume of measuring pipette	198.4 cc
Weight of N/4 solution formed	402.7 grams
Specific heat of N/4 HCl solution (Thomsen)	0.980
Rise of temperature (from Curve I)	
Final temperature	3.549°
Initial temperature	0.286°
Rise in temperature during experiment	3.263°

"Heat Capacity" of the solution:

$$402.7 \times 0.980 = 394.64 \text{ grams}$$

Total heat taken up by the solution:

$$394.64 \times 3.263 = 1287.7 \text{ cal}$$

One gram equivalent of sodium hydroxide (at a dilution of N/2) should liberate 13,740 cals. (Thomsen).

Then 198.4 cc of N/2 solution should liberate:

$$\frac{198.4 \times 13{,}740}{2000} = 1363 \text{ cals.}$$

The difference divided by the rise,

$$\frac{1363 - 1287.7}{3.263} = 23.07$$

is the water equivalent of the apparatus.

By a similar calculation we obtain from Curve II a rise of 3.261°, and a water equivalent for the apparatus of 23.33 grams. The mean of these two values is 23.2, and differs from each individual determination by but 0.6 percent. This reduces to a negligible quantity in the final calculations of heats of neutralization, *viz.*, 0.1 percent in the case of the half normal solutions, 0.025 percent for the normal ones, and 0.005 percent for the twice normal ones.

II. Method of Calculation of Heat of Neutralization.
(Neutralization of Normal Hydrochloric Acid with Sodium Hydroxide)

Temperature rise (from Curve III)	
Final temperature	24.678°
Initial temperature	18.130
Total rise in temperature during expt.	6.648°
Specific heat of N/2 NaCl solution (Thomsen)	0.964
Weight of NaCl solution formed	408.83 grams
Water equivalent of NaCl solution formed:	
$408.83 \times 0.964 = 394.11$ grams.	
Total water equivalent	$394.11 + 23.2 = 417.31$ grams
Total heat liberated	$417.31 \times 6.548 = 2732.6$ cal
Volume of sodium hydroxide actually neutralized	198.1 cc
1000 cc (containing one gram equivalent) would therefore liberate	
$\frac{2732 \times 1000}{198.1} = 13{,}793$ calories.	

The complete data for the determinations made on the four concentrations appear in the following table.

The results obtained for half normal solutions are somewhat lower than those given by Thomsen (Thermochemische Untersuchungsmethoden Vol. I) except in the case of nitric acid. The molecular heats of neutralization found at different dilutions exhibit little regularity of change; in the case of hydrochloric acid the value increases with the concentration; for nitric acid the value remains more nearly constant; for sulphuric acid it increases with the concentration; and for acetic acid the value diminishes from 13.2 + calories for fourth and half normal solutions to 12.9 + calories for twice normal solutions. Greater dilution than half normal seems to have little effect on the heat of neutralization.

As shown by the curves, the absorption of heat when working at even 10°–14° below room temperature is very small, amounting to less than 1/100° per minute. All of these determinations were made under unfavorable conditions, as they were all made in July when the temperature of the room was generally about 30°. Under ordinary laboratory conditions much better results could undoubtedly be obtained.

Strength of acid used	Heat of neutralization (in calories)	Average value
N/4 HCl	13,508	
N/4 HCl	13,565	13,536
N/2 HCl	—	(13,740)[1]
N HCl	13,791	
N HCl	13,785	13,788
2 N HCl	13,923	
2 N HCl	13,906	13,915
N/4 HNO_3	13,536	
N/4 HNO_3	13,561	13,548
N/2 HNO_3	13,648	
N/2 HNO_3	13,647	13,647
N HNO_3	13,612	
N HNO_3	13,616	13,614
2 N HNO_3	13,649	
2 N HNO_3	13,633	
2 N HNO_3	13,627	13,636
N/4 H_2SO_4	15,370	
N/4 H_2SO_4	15,353	15,361
N/2 H_2SO_4	15,585	
N/2 H_2SO_4	15,593	15,589
N H_2SO_4	15,674	
N H_2SO_4	15,667	15,670
2 N H_2SO_4	15,817	
2 N H_2SO_4	15,810	15,813
N/4 CH_3COOH	13,219	
N/4 CH_3COOH	13,244	13,231
N/2 CH_3COOH	13,231	
N/2 CH_3COOH	13,237	
N/2 CH_3COOH	13,233	13,234
N CH_3COOH	13,175	
N CH_3COOH	13,162	13,168
2 N CH_3COOH	12,903	
2 N CH_3COOH	12,943	
2 N CH_3COOH	12,921	12,922

[1] Reaction chosen for determination of water equivalent of apparatus.

It has been shown that the Dewar flask may be used successfully as a calorimeter for determining the heats of neutralization of acids and bases at widely different concentrations; heat radiation is very small, even when working considerably below room temperature, and results may be obtained which are concordant. By using but one vessel the acid and alkali acquire the same temperature and that temperature may be determined exactly. The working parts are simple, and if necessary can be made by a student of ordinary skill, thus making it both a convenient and reliable method for laboratory use in classes of physical and thermochemistry.

Laboratory of Physical Chemistry,
University of Wisconsin, Madison,
October, 1910

NEW BOOKS

Descriptive Meteorology. *By Willis L. Moore. 16 × 23 cm; pp. xiii + 344. New York: D. Appleton and Company, 1910.*—"The object in writing this book was to provide, so far as possible, the young men entering the service of the U. S. weather Bureau with a comprehensive introduction to modern meteorology."

The subject is discussed under the headings: the atmospheres of the earth and of the planets; atmospheric air; microörganisms and dust-motes of the air; physical conditions of the sun and its relation to the earth's atmosphere; heat, light, and temperature; thermometry; distribution of insolation and the resulting temperature of the atmosphere, the land, and the water; the isothermal layer; atmospheric pressure and circulation; the winds of the globe; the clouds; precipitation; forecasting the weather and the storms; optical phenomena in meteorology; climate. Concealed in one of these chapters—I will not say which—is a long and interesting dissertation on frost in cranberry bogs.

The book is full of items of interest to the physical chemist and to the frequenter of receptions. After reading this book one sees marvelous and unsuspected possibilities in the weather as a topic of conversation. It is perhaps too much to urge that this book should be on every dinner table; but there are times when that would be useful.

Among the briefer items of interest are: the variation in the amount of ozone, p. 14; the number of bacteria in the air, p. 27; the dust-motes in the air and how to count them, pp. 29, 37; the frost level in the free air, p. 93; our perplexity as to lightning, p. 169; the existence of supercooled water in clouds, p. 195; the limiting diameter of rain drops, about 0.3 inch, p. 208.

The author has the following to say, p. 67, in regard to the placing of thermometers. "In order that thermometers may indicate the temperature of the free air it is necessary that they be exposed where they will not receive direct radiation from the sun or sky or from surrounding objects, and where the air can circulate freely. They also must be protected from rain and snow as far as possible. In large cities it is necessary to locate the shelter on the roof of a building, if possible on one higher than any surrounding it, care being taken to avoid the influence of chimneys, skylights, ventilators, etc. Thermometers that are exposed to direct radiation from any source, even though they are protected from direct solar radiation, cannot indicate the true temperature of the air."

There are some curious facts about the temperatures in lakes, seas, and oceans, p. 84.

"Mill has shown that the lochs of Scotland, which are filled with sea water much freshened on the surface by numerous small mountain streams, cool on their surfaces as winter approaches, but, since the water is comparatively fresh, it continues to float on the warmer sea water below. The latter, because of its salinity, maintains a greater specific gravity than the chilled fresh water above. Convection does not operate freely, as it would if the lighter water were below. In many cases the water of these lochs is prevented from circulating with the cold water of the deep ocean by bars or sills which rise, at the entrance to the

loch, nearly to the surface. In such cases the fresh water may freeze, while the salt water that is below the level of the bar retains a temperature of 45° or more.

"Because of the displacement of oceanic isothermals by ocean currents, it is impossible to name a definite temperature as prevailing over oceans at all places on a given parallel of latitude. But in a general way it may be stated that at the equator there is a surface temperature of 82°–84° F, which changes less than a degree between day and night, and not over 5° between winter and summer; at a depth of 400 fathoms the temperature is 44° and unchangeable, and below 1,000 fathoms it is a little above the freezing point of fresh water—namely, 34°–36°. In the middle latitudes the surface variation is from 50° in winter to 68° in summer. At latitude 70° N the surface temperature has but a small diurnal variation, and a yearly range of from 35° for winter to 45° for summer; at a depth of 400 fathoms it remains steady at 32°. From this level there is a gradual decrease to a depth of 1,000 fathoms, where a constant temperature of about 28° exists, and below this to the bottom there is no change. One may get an idea of the enormous volume of cold water that lies upon the surface of the earth from the statement that about three-fourths of the earth is covered with oceans, whose depths average about two miles, and in some places five miles, and whose temperatures below one mile are always close to the freezing point.

"The temperature of enclosed seas is fairly well represented by the thermal conditions of the Red Sea, which extends in a nearly north and south direction, approximately one-half of it lying in the tropics, being 1,450 miles long and about 180 miles wide. It receives heat from the hot radiating land that confines it to a long channel, which is narrow in comparison with other inland seas. Only the surface water of the Indian Ocean on the south is able to enter to take the place of the large amount that evaporates, for at its southern extremity a bar or sill, which extends from the bottom to within 200 fathoms of the surface, separates the deep water of the sea from that of the outside ocean. Its surface temperature varies from 85° in summer to 70° in winter, which is about the same as that of the Indian Ocean. Both bodies decrease in temperature at about the same rate down to the level of the sill, where the temperature remains constant at 70° the year through. Here their thermal similarity ceases, for the Red Sea, which has a depth of 1,200 fathoms, maintains a temperature of 70° from the top of the sill all the way down to the bottom, while the ocean continues to decrease in temperature down to a depth of at least 1,000 fathoms, where a temperature of 34°–36° F prevails without variation.

"In a comparison between the Mediterranean and the basin of the Atlantic, a similar condition is found to exist. The sill at the entrance to the Mediterranean is 190 fathoms below the surface, at which level the temperature of both bodies is equal to 55° F. In the Mediterranean this temperature continues clear down to the bottom, while the temperature of the Atlantic at the same level as that of the bottom of the Mediterranean is only 35°.

"In Lake Superior, which has an average depth of 900 feet, the temperature below the level of 240 feet remains unchanged throughout the year at 39°."

On p. 100 we learn that mountain tops are cooler than free air at the same level.

"Wherever observations have been made they have shown that the tem-

perature of the air on high mountain peaks and crests and for a distance of 100–300 feet above them is appreciably cooler than adjacent free air of the same height, due to deflection of the winds and radiation of the peaks. It is, therefore, probable that the same conditions of coldness prevail over all mountains. Clayton, in an excellent series of observations at Blue Hill, Mass., has shown that even at this station, which is only a little over 600 feet above the sea level and 480 feet above the level of the valley, the temperature at night is lower than that of the free air at the same elevation over the valley, the difference often being as much as 2°, 5°, or 7° F; and when the decrease of temperature with elevation in the free air was less than the adiabatic rate, as it usually is, the cooling appeared above the top of Blue Hill in the daytime. When the kites were pulled in at night the kite-meteorograph generally showed a uniform rise of temperature with descent until it was within less than 150 feet of the top of the hill, when a sudden fall of temperature occurred. The mean temperature of the air above every peak that has been compared with the temperature of the free air of the same level has been found cooler than the free air, and it is probable that all mountains, by forcing the air to rise over them and to cool by expansion as it ascends—which cooling usually is at greater rate than the vertical decrease of temperature of the free air—produce a cooling effect that more than compensates for the heat given to the air by conduction and radiation from the mountain. This effect must be greater when the direction of the wind forms a considerable angle with the direction in which the mountain trends, and be greatest when the incident winds encounter mountains at right angles to their direction of movement. On clear nights mountains are abnormally cooled by radiation."

On p. 105 the author compares the temperature changes for San Francisco, Denver, Chicago and New York.

"San Francisco, being situated near the ocean and in the prevailing westerly winds of the middle latitudes, has a marine climate, the westerly wind usually bringing to that city the temperature, approximately, of the ocean. The range of the temperature of the water is not great, and consequently there is found on the Pacific Coast very even temperature. The range at New York should be greater because of its position farther north, but were the prevailing winds from the Atlantic on the eastern seaboard, the range in temperature would not be materially greater than along the Pacific Coast. Temperature conditions at New York are therefore affected somewhat by the proximity of the ocean, and the range is consequently considerably less than in the interior. Denver, Colo., located at a slightly lower latitude than New York City, has a much greater annual range in temperature, and it is even greater than Chicago, the temperature in the latter city being affected by the great lake that washes its shores, but while its annual range is considerable, it is not as great, as a rule, as that observed on the great plains, immediately east of the Rocky Mountains, or on the same parallel of latitude, where it approaches close to the Pacific Ocean, but is partly protected from the modifying vapor of the ocean by intervening high mountain ranges."

Some interesting facts in regard to marshes and bogs are brought out on p. 108.

"In order to ward off frost, progressive cranberry growers have resorted to

three expedients, *viz.*, cultivation, drainage, and sanding. Through cultivation the marsh may be kept clean and free from weeds, moss, or other rank growth, thus permitting the solar radiation to reach the soil and to increase its temperature. The growth of thick vegetation screens the soil from the sun's rays, and there is consequently less heat in such a soil to be given off by radiation or conduction in the nighttime. Drainage lowers the specific heat of the soil and decreases the cooling effect of evaporation; therefore, under sunshine the dry soil becomes warmer than the wet and, whether or not it has *more* heat to give off at night, it has a higher temperature and therefore radiates more freely to the air above. A covering of sand likewise lowers the specific heat of the surface, and thereby conduces to a higher temperature during the day and increased radiation at night. In the Cape Cod cranberry marshes sand about half an inch in depth is spread over the surface of the bog each year, while in Wisconsin no such systematic method has been adopted; but several of the marshes have been sanded from time to time, usually to a depth of about 2 inches, at intervals of several years. These three methods of preventing low night temperatures have been so beneficial that where systematically carried out, there is practically no need of flooding to prevent frost, except in the spring or autumn.

"The cold air, on nights when frost is imminent, settles gradually down the slopes to the bottom lands, and if all the conditions in these bottom lands or bogs were the same, there would be no differences in air temperatures at the surface; yet it is interesting to see how much the temperature varies at different places in the same bog, and often even when these places are near together. The difference in temperature over these various surfaces disappears often at an elevation of 3 feet, while at the very surfaces there may be a difference of from 5°–10°. The cold air, as it settles gradually through gravity, overspreads the marsh, but here and there we find warm places and cold places, and still others having an intermediate value. This variation in temperature is due largely to the differences in temperature of the soil or covering. It is as if heaters of varying power were scattered over the bog, giving off heat to the air immediately above, some in greater quantity, others in less. In places where the heater was protected by vegetation and, therefore, not supplied with much fuel the previous day, or where, much heat being supplied, the specific heat of the heater was so great that but little gain in temperature was effected, or where the fuel was consumed in processes other than those of heating, such as evaporation, there is weak radiation at night; at those places the surface air temperatures remain relatively low. Right here it is important that a close distinction be made between the effect on the air of weak radiation and conduction from a surface of great specific heat and moderate temperature and the effect of rapid transference of heat from a good conductor having a surface of low specific heat and high temperature. In the first instance, a moderate amount of heat may be transmitted for a long time without addition to the original quantity; in the second case, comparatively high temperature is transmitted for a short time, which period, however, may be sufficiently long to span the hours at night when frost is liable to occur."

On p. 121 we learn that "we therefore have two distinct strata in our atmosphere that intermingle but slightly: a lower or inner turbulent one, which includes the first two regions previously described, with a large negative tempera-

ture gradient, and an upper or outer one, with a small positive gradient, floating on the first, like oil on water. The lower stratum contains from two thirds to three fourths of the entire mass of such gases of the air as oxygen, nitrogen, and all the members, except helium, presumably, of the argon family; a still greater proportion of the carbon dioxide, and nearly all the water vapor. It is warm in its lowest portion, but cools, irregularly at first, then rapidly and nearly regularly, with increasing elevation to a minimum of from —40° to —70° C. The upper stratum contains extremely little water vapor, and its temperature rises, sometimes abruptly at the start and then slowly, but usually slowly all the way, with elevation from the place of inversion to an unknown temperature at a height not yet reached. Occasional observations indicate an isothermal condition, and for this reason the outer atmosphere is often called the *isothermal layer*, and a few observations have shown even a slow cooling with elevation, but both these conditions are unusual.

"The region above the upper inversion cannot appreciably be penetrated by convection currents from the air below, since this would cause a cooling by expansion of the rising mass to a temperature lower than that of the surrounding medium, so that under the same pressure or at the same level its density would be greater than that of the adjacent air; and therefore all storms, all condensation, all abnormal and irregular moisture distribution, and virtually all dust, except that of meteors and of violent volcanic eruptions, are limited to the lower atmosphere."

It will perhaps be news to some to learn, p. 145, that North America is the principal breeding ground for storms.

"Any theory to explain the origin of cyclones and anticyclones must account for the fact that Asia is singularly free from such disturbances. The great Himalayan range runs east and west near the southern part of this continent, and, naturally, interferes with the flow of currents of air from the Indian Ocean to the interior. On the other hand, in North America the Rocky Mountains run north and south along its western portions, and, while they tend to check the eastward flow of air in the lower strata, they permit the flow of warm currents from the south and cold currents from the north over the United States. Therefore, in Asia the mountains tend to prevent the conflict of currents that seem to be necessary to the formation of cyclones, while in North America they aid it. Hence it is that North America is the region of the most vigorous mixing processes in the northern hemisphere, and, in fact, in either hemisphere, and is the area upon which the most active cyclonic circulation takes place; for this reason it must be the special theater for meteorological studies upon the causes and effects of the thermodynamic and hydrodynamic forces operating in the lower strata of the atmosphere."

The author groups the winds of the globe, p. 177, under three general headings, as follows: permanent winds, periodic winds, and non-periodic winds.

"To the permanent winds belong the trade winds, the antitrades, and the prevailing westerlies of high latitudes; to the periodic winds belong monsoons, land and sea breezes, and mountain and valley breezes; to the non-periodic winds belong the high winds that accompany cyclones and anticyclones, including the hurricane of the West Indies, the typhoon of the China Seas, the simoom of Arabia and Africa, the sirocco of Italy, the föhn winds of the Alps,

the chinook winds of the northwestern part of the United States, the mistral of Europe, the Texas northers, the blizzards and the hot winds of our western plains, tornadoes, thunderstorm gusts, whirlwinds, and many others."

The author has the following in regard to the chinook winds, p. 186.

"In North America when an area of low pressure crosses the Canadian Rockies, it causes winds from the Pacific to cross the mountains in its southern quadrant. These cause copious rains or snows on the western slopes of the mountains, and hot, dry winds to the east of them. Since the prevailing winds of this region are from the west, these winds at certain seasons become almost permanent, and exert a marked influence on the climate, which is particularly noticeable in the Saskatchewan valley in Canada and in portions of Montana and Wyoming in the United States, where the winters are noticeably milder than on the corresponding parallels farther east. The valleys are generally free from snow, so that stock can live on the ranges practically the entire year.

"While the effects of the chinook winds are most marked in the valleys on the eastern slopes of the Rocky Mountains, they are sometimes felt 500 miles to the east of them. They are also noticeable as far south as Colorado. We should expect to find traces of their influence in the vicinity of all extensive mountain ranges outside the tropics."

There are apparently some clouds which puzzle the meteorologists a good deal, p. 197.

"Certain clouds that are seen about midnight in summer have for twenty years past received considerable attention from Abbe and others, but as yet we do not know enough about them to give them a name; sometimes they are called nacreous, from their gentle, pearly luster, at other times noctilucent, because they shine at night; they have as yet only been observed in northern latitudes during the month of June and above the northern horizon. The most reasonable assumption is that they are so high up as to receive a little light from the twilight then prevailing over the Artic regions. Otherwise they may be self-luminous or phosphorescent.

"A few measurements have given these clouds altitudes of between 20 and 40 miles. But we believe that a more systematic search for such clouds and a more careful determination of their altitudes must be made before we can attempt to discuss the questions that will naturally arise in regard to them, for of course at present no one can understand how aqueous vapor can be carried up to those altitudes or exist there long enough to form a visible cloud. The eruption of Krakatoa did throw vapor particles up to middle altitudes, and these formed interesting optical phenomena, but not visible clouds. However, if such clouds do exist, and their motions can be determined, we shall hardly dare to assume that the motions represent any movement of the atmosphere as such, for the air is so rarefied that the cloud particles may be moving without reference to the wind."

It is quite clear where the author stands in regard to rain making, p. 206.

"The hypothesis suggested centuries ago that any loud noise, such as thunder or cannonading, or even the ringing of bells, jostled the small drops together so as to form large ones and rain, was fully disproved by the experiments made at the United States Government's expense in 1892. An appropriation for this work was made by Congress in deference to a widespread popular de-

mand that something be done to relieve the dryness of our arid regions and our droughty summers. Several popular writers had diffused the illogical conclusion that since great battles are frequently followed by rain,[1] therefore the noise of the cannon or the clashing of swords against coats of mail had caused the formation of raindrops.

"In the government tests heavy charges of explosives, such as dynamite and rosselite, were carried aloft and even into the interior of clouds by means of kites, and balloons, and exploded there, but with no resulting rain. Similar experiments were made by others, and some tried even the foolish method of the fakirs, who send small quantities of gas or vapor into the air. But the general result is that no rain has as yet been brought down from the clouds by any human agency.

"The ringing of church bells has for ages been practiced in southern Europe as a method of preventing hail, although the foolish practice was forbidden long ago by papal decree. Of late years a form of hail cannon has been widely employed in parts of Europe for shooting vortex rings of smoke upward, under the impression that such rings would break up the ascending or gyrating currents that are supposed to make hail. But it has been abundantly shown by Professor Pernter and others that such vortex rings have no appreciable influence on the formation and path of a hailstorm.

"The lightning rod of Benjamin Franklin, originally intended to protect from destruction by lightning, was afterwards assumed to protect also from the hail which accompanies thunderstorms. But the collected statistics do not confirm this assumption."

On p. 222 we read that the winter storms are general rather than local, whereas the reverse is more often the case in summer. "The summer type of local storms gradually merges into general storms as the heat of summer wanes, the first general rain-storms usually occurring during the latter part of September. This has given rise to the erroneous idea of an equinoctial storm."

On p. 223 we find a statement of the conditions for forming a hot wave.

"In summer there come periods of stagnation in the drift of the highs and the lows. At such times, if a high sluggishly rests over the South Atlantic Ocean between Bermuda and the coast of the United States and a low over the northern Rocky Mountain region, there will result what is popularly known as a warm wave, for the air will slowly and steadily flow from the southeast, where the pressure is greater, toward the northwest, where the pressure is less, and, receiving constant accretions of heat from the hot, radiating surface of the earth, without any cyclones to mix the upper and lower strata, will finally become abnormally heated. This superheated condition of the lower stratum continues until the high over the ocean dies out or drifts away to the east and the low-pressure area in the northwest begins to gyrate as a cyclone and moves eastward, mixing in its course strata of unequal temperatures and causing cool thundershowers."

It is interesting to learn, p. 233, that "four sevenths of all the storms of the

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[1] Probably because they usually begin on fair days, and rain falls one day in three at least, on the average, in any region populous enough to mobilize any considerable fighting force.

United States come from the north plateau region of the Rocky Mountains and pass from this subarid region eastward over the Lakes and New England, producing but scant precipitation. The greater number of the remaining three sevenths are first defined in the southwest States or territories. These nearly always can be relied on to cause bountiful precipitation as they move northeastward over the lower Mississippi Valley and thence to New England.

"Droughts in the great wheat and corn belts and elsewhere eastward are broken only by cyclones that form in Arizona, New Mexico, or Texas.

"Storms move faster in the northern part of the United States than they do in the southern portion, and their tracks migrate with the sun."

Although most people use cyclone and tornado as synonymous terms, this is quite wrong, p. 238. "The cyclone is a horizontally revolving disk of air, probably 1000 miles in diameter, while the tornado is a revolving mass of air of only about 1000 yards in diameter, and is simply an incident of the cyclone, nearly always occurring in its southeast quadrant. The cyclone may cause moderate or high winds through a vast expanse of territory, while the tornado, with a vortical motion almost unmeasurable, always leaves a trail of destruction in an area infinitesimal in comparison with the area covered by the cyclone."

One pre-requisite for a tornado is an abnormal heating of a thin stratum of air next the earth, while the stratum next above still retains the cold of winter. This accounts for tornadoes occurring usually early in the afternoon of a spring day. This abnormal heating causes an unstable equilibrium, p. 239, which "is more often relieved by the breaking through, here and there, of masses of the heavier air and the ascent of the lighter together with a *horizontal* rolling along the surface of the earth; these are *thunderstorms*. But at times a narrow *vertical* whirl is set up which develops great vortical energy; this is the tornado."

"Tornadoes mostly occur between 2 and 5 in the afternoon, and generally move from the southwest to the northeast; their tracks may vary in width from a few hundred feet to one mile; their velocity of translation is usually about that of an express train; their speed of gyration can be measured only approximately, but it is sufficient often to drive straws into the bark of trees. A roaring sound like the sound of many express trains accompanies the tornado, whose track is usually 5 or 10 miles in length."

The sky of the novelist may be blue or red or yellow or some other color; but it is rarely, perhaps never, green. The reviewer recalls distinctly being taken severely to task, many years ago, for saying that the sky was sometimes green. The Chief of the Weather Bureau is not so intolerant, p. 245.

"In the lower half of the atmosphere there are frequently larger particles, probably of aqueous vapor, dust, and smoke that absorb the blue, but transmit the red, so that after sunset or before sunrise beams of reddish light permeate the atmosphere above our heads. When we look at this light directly above the sun and at an altitude of from 10°–20° above the horizon, while the sun is 10° or 15° below the horizon, we see a pinkish blotch on the sky; on either side of this for a long distance we perceive a delicate green tint shading above into the blue and below into the yellows and reds. Lower down nearer the horizon, both before and after sunset, we frequently see horizontal bands of both red and yellow, the red being more prominent in warm, moist air, and the yellow in cold, dry air. In very dry air, such as occurs in areas of high barometric pressure and cloud-

less skies, the color is a light lemon-yellow, but this is only seen in temperate and northern latitudes, while the deeper yellows and reds prevail in the tropical regions and in our moist summers and on the advancing fronts of areas of low pressures or storms."

The section on the colors of clouds, p. 254, is worth quoting in full.

"An observer inside a bank of fog usually reports that the sky is cloudy and of a gray tint, since this is about the character of the light that penetrates the bank of fog, unless it be a very light fog or haze, or he be near its surface. There is quite a distinction between the tints seen inside a wet fog or cloud and those seen inside a dry fog or haze, such as is always associated with the harmattan on the west coast of Africa. In the latter case the sky has a chalky-white tint and the air is very dry. We attribute the whitish tint not to any moisture, but to the presence of innumerable fragments of microscopic diatoms or siliceous shells. The whitish color of the haze must be attributed to the reflection of light from their surfaces. A similar white haze occurs in air that is full of grains of pollen, or fine crystals of snow, or almost any other kind of small particles.

"Although the clouds appear white in full sunlight, yet when illumined by the yellow and red rays that penetrate to them from the setting sun they form the most magnificient color displays that are to be found anywhere in nature.

"The upper part of a tall cumulus is often a delicate pink, while the lower portion is ashen gray; and below that the blue and green sky tints may be visible. A decided pink or straw-colored yellow is often seen when looking at the dazzling white on the sunny side of a cumulus cloud. Apparently the surface particles of the cloud are being evaporated in the sunshine, and the adjacent layer of air is supersaturated with moisture at a relatively high temperature; possibly minute particles of water are present and modify the orange and pink that are spread in spots over the cloud. The tints are only seen when cumuli are sending up great thunderheads like explosions of steam boilers.

"Still another color phenomenon is associated with the under sides of cumulus clouds, as in approaching thunderstorms, when the landscape beyond the cloud is brilliantly lighted by the sunshine; in such cases the observer may see patches of yellow or green on the lower side of the cloud, being light from the bright landscape, reflected by the big drops."

We are grieved to read, p. 266, that the Gulf Stream is not so important a factor in the English climate as we had always supposed.

"In this connection the writer would correct what he believes to be an exaggerated popular idea relative to the effect of the Gulf Stream on the climate of Europe. The eastward extension of the Gulf Stream—generally known as the Gulf Stream Drift—doubtless brings immense quantities of relatively warm water to the shores of western Europe; but that the latter region is warmer, more humid, and less subject to radical changes in temperature than equal latitudes in North America, except on the Pacific coast, is due primarily to the mere presence of a great ocean to the westward and the prevalence of westerly winds. Without ocean currents of any description this body of water would give to the air that moves from it to Europe a mild and damp climate and a more equable temperature than is possessed by the eastern part of the North American continent."

Those who are interested in mean temperatures as a test of climate should read the paragraphs, p. 268, on an equable climate.

"Within the broad confines of the United States there are many, but not all, shades and varieties of climate. One of the questions most frequently asked is: "Where shall I find a climate possessing both dryness and equability of temperature?" To this interrogatory reply must be made that the ideal climate as regards equability of temperature and absence of moisture does not exist, but that a near approach to it will be found in the southwest part of the United States.

"The temperature of the Southwest is not equable in the sense of having an extremely small daily range, but it possesses the quality of annual uniformity in a greater degree than will generally be found elsewhere, except on the sea-coast, and there the humidity is great.

"The most equable temperature on the globe will be found on the high table lands and plateaus of the tropics. Bogotá, in the United States of Colombia, has an average temperature of about 59° F for all months of the year, and the range for the entire year is less than is often experienced in a single day in some parts of the middle latitudes. But while the ideal temperature may be found on the higher elevations of the tropics, the rainfall is much greater and more continuous than in this country.

"At sea level in the tropics extreme conditions of heat and moisture produce great physical discomfort. But even under the equator it is possible to escape the tropical heat of low levels by ascending from 4,000–6,000 feet. In the economy of nature there is a certain limit beyond which the two extremes, dryness and equability of temperature, cannot coexist; thus we may find a region so deficient in moisture as to satisfy the requirements of the case, but the very lack of moisture is a condition that facilitates radiation and thus contributes to extremes of temperature.

"Regions may be found, as on the lower Nile, where there is a lack of rainfall coupled with a high and moderately uniform temperature. The mean winter temperature of Cairo, Egypt, is 56° F; mean summer temperature, 83°; a range from winter to summer of 27°. The mean winter temperature of Phoenix, Arizona, is 52°; mean summer temperature, 87°; a range of 35°. It is, therefore, by no means difficult to find a counterpart of the far-famed Egyptian climate in the great Southwest."

As a chemist, the reviewer protests against the term "atmosphere" being used, p. 14, as synonymous with "gas." "The earth is surrounded by four important atmospheres—nitrogen, oxygen, vapor of water, and carbon dioxide." The paragraph accounting for cyclonic action, p. 160, is so vague and unsatisfactory that it might well have been left out. *Wilder D. Bancroft*

Essentials of Chemistry. *Experimental, Descriptive, Theoretical. By Rufus Phillips Williams. 13 × 20 cm; pp. ix + 421. Boston: Ginn and Company, 1910. Price: $1.25.*—The title of this book is an attractive one, but the author has been so careless in many of his statements that the value of the book is much impaired thereby.

On the first page he says that "chemistry may be defined as that science which treats of matter in its simplest forms, and the various combinations of

those forms." While this definition may be justifiable, there is really no reason why the student should be made to memorize it at the start as a fundamental definition. Incidentally the definition of matter does not come until the next paragraph.

At the bottom of the same page—the first one—we are told that "whenever there is matter in motion—and it is everywhere—work is being done, and that which does the work we call *energy*, though it is a subtle, invisible worker, which we know only by its effects." It is not worth while to speculate as to what the author means by this, but it does seem cruel that any student should be asked to memorize this as a fundamen al definition.

On page 4 we find the interesting statement that "a molecule is the smallest particle of an element or a compound which can be separated from a mass by physical means. It retains most of the properties of the mass of the substance."

On page 6 the author says that "When sugar is dissolved in water, the result is called a *mixture* of the two substances. If sulphur and iron particles are stirred together, the result is a mixture." It does not seem credible that anybody could treat these two cases as analogous.

Speaking of chemical affinity, p. 6, the author says that "at very high temperatures compounds are often broken up. At extremely low ones reactions scarcely take place." It seems probable that the author does not distinguish between chemical affinity and reaction velocity.

On page 22, we read that "a molecule is a group of atoms held together by chemical affinity. The molecules of a given substance always contain the same kind of atoms and the same number, but those of different substances have usually different kinds of atoms and varying numbers." If one admits that red and white phosphorus, for instance, are different substances, this statement may stand; but if this statement is the criterion of a substance, why not say so?

On page 154, the author tries to define saturation, and of course comes to grief. "When a solvent holds in solution all of a given solid or gas that it can retain, it is said to be saturated." This sounds well but how much gas can a solvent hold in solution? That depends entirely on the pressure, to which no reference has been made.

Under efflorescence and deliquescence, page 155, there is nothing to show what the decisive factor is. On page 214 is the startling statement that "electrolytes of the first class are usually metals." The author does not distinguish between a conductor and an electrolyte. It is quite evident that he has never read Faraday, but if further proof were needed, it is to be found page 218, in the statement that the "metallic or positively charged ions are attracted to the cathode."

On page 217, the author says that "the more dilute a solution, up to a certain point, the greater the conductivity." This is not true; the author means molecular conductivity.

There is a most extraordinary statement on page 218. "In order to have equilibrium it is evident there must be the same number of negative as of positive ions in a solution. This serves to explain why a salt readily soluble in water is not so soluble in water containing other compounds having some of the same ions in solution; for example, on adding hydrochloric acid to a strong solution of barium chlorid, a precipitate of barium chlorid is formed. This is usually

explained by saying that $BaCl_2$ is less soluble in HCl than in water; the ionic explanation is that there is an excess of chlorin ions when HCl is added to $BaCl_2$, equilibrium is upset, and hence a precipitate continues to fall until equilibrium is again asserted."

The author's definition of a reversible reaction seems to be page 219, a reaction which runs to an end in one direction at one temperature and to an end in the other direction at another temperature.

When a sulphate is electrolyzed, the author states, pages 225, 228, that the SO_4 ion breaks down into O and SO_3, the sulphur trioxide combining with water to regenera:e sulphuric acid. This is very possibly true, but it is not an accepted doctrine outside of France. If the author can prove his statement, he should present his evidence.

The Moissan furnace, page 230, is not "a general type of most electric furnaces;" the temperature of the calcium carbide furnace is certainly not 3300° in any resistance type. In the Castner-Kellner process, page 232, the NaCl is not "fused by the current, +, +, of the anode."

The reviewer doubts whether nowadays, page 323, "phosphorus is obtained mainly from bones of vertebrate animals." It certainly is never "made by the electrolytic process," page 324.

On page 379, the author says that white lead "is a basic carbonate of varying composition, *e. g.*, $2PbCO_3.Pb(OH)_2$". This is self-contradictory. If white lead were really a substance of varying composition, no definite formula could be written for it.

It is certainly a desirable thing to include some physical chemistry among the essentials of chemistry, but it is a great pity that good intentions should be accompanied by such a painful degree of ignorance. It is better to have no physical chemistry at all than to have so much which is not so.

Wilder D. Bancroft

Verhalten der wichtigsten seltenen Erden zu Reagentien. By *Jos. v. Panayeff. 14 × 22 cm; pp. iv × 83. Halle: Wilhelm Knapp, 1909. Price: paper, 3.60 marks.*—What is a rare-earth? That is an interesting technical question, which has caused no little patento-legal perturbation. The term is applied to the oxides of certain elements which are classified into two groups, namely, the cerite metals and the yttrite metals, so classed according to the solubility of the double sulphates (with alkalies). The oxides of thorium and zirconium are often associated with these for reasons unnecessary to give here. The "rare-earths," about twenty five percent of the accepted list of chemical elements, whose names have some far-off meaning to a vast majority of chemists, are not so rare after all. In fact some are more common and apparently occur in greater abundance than many elements spoken of with the greatest intimacy. The cause of this is not difficult to find. The methods of separation and identification are not easy nor over-definite, except with a few cases. A dependable manual would therefore be most acceptable. Several small books are available. Each has its worthy features, but none is satisfactory, hence the reviewer welcomed this small book with hopes. Again there was disappointment. The authors of the several books are not altogether at fault, because the methods are not yet worked out; but some have been worked out which are not incorporated.

For instance one might wonder why the conduct of thorium with fumaric acid (*Miller and Metzger*); *with potassium trinitride* (*Dennis*), *and the behavior of* zirconium salts with sulphurous acid and their separation from titanium (Baskerville)—methods developed in the United States with material found in quantity within its territory, are not mentioned, except for the fact that the author states that the minerals from which these elements are extracted are found in Norway Sweden, Brazil, Canada, Russia "und anderen Ländern." In short, the literature has not been covered. This resident of St. Petersburg starts out with the periodic classification, but he has not read Mendeljeff's "Principles," or if he has, it did not profit him much in preparing his booklet, for therein he would find not a few facts that he has failed to incorporate. In his revision, which, it is hoped, will develop an index, we commend a careful study of Böhm's excellent compendium. The book would then acquire real value, for it is quite good as far as it goes, but it doesn't go far enough. *Charles Baskerville*

L'Energie. *By W. Ostwald. Traduit de l'allemand, par E. Philippi.* (*Nouvelle Collection scientifique. Directeur: Émile Borel*). *12 × 18 cm; pp. x + 237. Paris: Félix Alcan, 1910. Price: paper, 3 fr. 50.*—In the first chapter Ostwald takes up the preliminary work of Aristotle, Archimedes, Galileo and Lagrange. The second chapter deals with perpetual motion and the third with motion. In this third chapter the references are chiefly to Galileo, Newton, Huyghens, and Leibnitz. The fourth chapter is devoted to the mechanical equivalent of heat, and Ostwald quotes Mayer's first paper in full. In the fifth chapter we get Sadi Carnot's work on the steam engine together with the formulation of the second law of thermodynamics by Clausius and by Thomson.

Ostwald calls attention to the fact that Sadi Carnot was twenty-eight years old when his paper appeared and that Mayer, Joule, and Helmholtz were twenty-five, twenty-six, and twenty-five years old respectively, when the papers on the mechanical equivalent of heat and on the conservation of energy were published He uses these facts as an argument against extending the education in the secondary schools over too long a time.

The remaining chapters are entitled: energy and entropy; energetics; the law of intensities; the capacity factors; life; psychological phenomena; energetics and sociology.

Ostwald cannot resist a fling at the mechanical hypothesis, pp. 120, 127. "The mechanical hypothesis has two very serious disadvantages. It forces us to adopt a large number of secondary hypotheses which cannot be proved, and it is powerless to account for what our daily experience shows to be a fact, the relation between physical phenomena in the narrow sense of the word and psychological phenomena.

"All the mechanical explanations of the different forms of energy have, sooner or later, proved insufficient. They are now abandoned in many branches of physics. People have begun to replace them by electrical hypotheses; but those who remember the fate of electrical hypotheses in chemistry will not be very sanguine as to what they may accomplish in physics."

In the chapter on life, page 178, Ostwald says that "a constant manifestation of energy is an essential characteristic of life, even though this may not serve as a complete characterization."

On page 181, he says: "It is important to note that the idea of conservation can be taken in two different ways, the conservation of the individual and the conservation of the race. Usually whatever is good for the individual is good for the race and *vice versa*, but sometimes the contrary is true. In such cases what assures the perpetuation of the race is more in harmony with the biological tendency than that which assures the perpetuation of the individual. Under some conditions the race may go on though the individual perishes, for instance if the individual dies after reproducing its kind. If the race disappears the biological goal has not been reached even though the life of the individual be prolonged."

The translation has been done well enough, but it lacks the clearness and vivacity of Ostwald's prose.

Wilder D. Bancroft

Les Etats Physiques de la Matière. *By Ch. Maurain. (Nouvelle Collection scientifique. Directeur: Émile Borel.) 12 × 18 cm; pp. 323. Paris: Felix Alcan, 1910. Price: paper, 3.50 francs.*—The subject is treated under the following headings: the gaseous state and ionization in gases; the liquid state; crystals and the crystalline state; general structure of solids; inversions of solids, and solidification; anisotropism produced by external actions; flowing crystals, liquid crystals and crystalline liquids; properties of surface films and of thin layers of solids; homogeneous mixtures; heterogeneous mixtures; colloidal state.

This book is merely a compilation and is noticeably lacking in inspiration.

Wilder D. Bancroft

THE REPLACEMENT OF THE METALS IN NON-AQUEOUS LIQUIDS AND THE SOLUBILITY OF METALS IN OLEIC ACID

BY CHARLES BALDWIN GATES

SOCIÉTÉ CHIMIQUE DE FRANCE ANNULÉ

INTRODUCTION

About four years ago, Sammis[1] showed that certain types of chemical reactions that take place in aqueous solutions that conduct electricity can be duplicated in non-conducting liquids. That this is true of most of the typical chemical reactions has been demonstrated by the work of Kahlenberg and others.[2] Even the replacement of one metal by another in a non-aqueous medium has been shown to take place in liquids that are the best of insulators. Thus it has been proven that chemical reactions do take place in non-conductors and that these reactions are in every respect the same as to type and rapidity as those occurring in aqueous solutions.

The present research has for its aim the further investigation of this new field of chemical replacement of the metals in non-conducting media. If a large number of such replacement experiments be performed, using all the more common metals, the relative frequency with which these will replace some one metal, as copper for instance, may fairly be used as a basis for the arrangement of the metals in a series analogous to the so-called electrochemical series. Such a series would throw some light on the question as to whether the relative basicity of the metals is always approximately the same and an inherent property of the individual metals, or whether the nature of the solution in which the replacement is effected must be considered.[3]

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[1] Jour. Phys. Chem., 10, 593 (1906).

[2] Kahlenberg: Ibid., 6, 6 (1902); Kahlenberg and Schlundt: Ibid., 6, 447 (1902): Mathews: Ibid., 9, 641 (1905); Kahlenberg: Zeit. phys. Chem., 46, 63 (1903).

[3] Compare Kahlenberg: Science, 31, 41 (1910).

It has been particularly emphasized by the adherents of the electrolytic dissociation hypothesis that there is a close connection between the electromotive forces set up by metals in contact with solutions of their salts on the one hand and their replacing power on the other hand. Unfortunately, the experiments which seemingly confirm this view have been limited to electrolytic solutions in which water was the solvent, as a rule. A complete series of replacements, obtained in solutions that are insulators, would have a distinct bearing upon the question as to whether the relationship between the replacing power of the metals and the electromotive forces which they may develop really exists. Accordingly, the following experimental work was undertaken in order to determine in a large number of cases what metals will replace each other in non-conducting liquids.

GENERAL PLAN OF THE WORK

The replacement of copper by other metals was chosen for this investigation and consequently some pure copper salts were necessary. But as non-aqueous solvents were to be employed, inorganic copper salts could not be used, for they are insoluble in such liquids, as a rule. Organic salts were therefore taken and salts with considerable carbon content were preferred, in order that the large organic radical might more readily drag the copper into solution in the organic solvents[1] to be employed.

Pure anhydrous solvents were then carefully prepared and the solubility of the copper salts determined in them. The conductance of the pure solvent and of the solution was measured in each case. In the concentrated solutions so obtained, strips of the metals were introduced and all replacement indications were carefully noted. The work was done at different temperatures and prolonged for various periods of time. The effect of small amounts of moisture upon the reaction was also duly investigated.

[1] Kahlenberg: Trans. Am. Electrochem. Soc., 6, II, 53 (1904).

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The replacement of copper in non-conducting fused salts and the replacement of other metals in fused salts that do conduct was studied to determine whether the presence of water is necessary for chemical action to take place. These experiments also furnished a replacement series which could be compared with the ordinary electrochemical series of the metals and so aid in determining whether the relative replacing power of each metal is constant.

The accidental discovery of the solubility of metallic copper in oleic acid led to the preparation of some very pure oleic acid and the investigation of its ability to dissolve metals. This was an unexpected development on account of the fact that the higher fatty acids are complete insulators.

EXPERIMENTAL WORK

Preparation of Copper Salts

The salts were all prepared in aqueous solutions by neutralization of the free acid with caustic potash and subsequent precipitation of the copper salt with a solution of pure copper sulphate. These salts were then thoroughly washed and dried to constant weight at a temperature as close to 120° C as the salt would bear without decomposing.

Copper anisate—$(C_6H_4(O.CH_3)COO)_2Cu$—was green. Copper margarate—$(CH_3\text{-}(CH_2)_{15}\text{-}COO)_2Cu$—was blue when first precipitated, but it changed to a dark green at about 100° C. Copper cinnamate—$(C_6H_5\text{–}CH = CH\text{—}COO)_2Cu$—was bluish-green. Copper phthalate—$C_6H_4(COO)_2Cu$—was sky-blue and precipitated only on evaporating the solution to a small bulk. Copper abietate—$(C_{18}H_{29}COO)_2Cu$(?)—was light green and was prepared from abietic acid extracted from Oregon balsam. Copper camphorate—$C_{10}H_{14}O_4Cu$—was bright green and in an exceedingly fine state of division.

The following copper salts were furnished by Professor Kahlenberg: copper palmitate—$(CH_3\text{—}(CH_2)_{14}\text{—}COO)_2Cu$—made by J. L. Sammis; copper laurate—$(CH_3\text{—}(CH_2)_{10}\text{—}COO)_2Cu$; copper capronate—$(CH_3\text{—}(CH_2)_4\text{—}COO)_2Cu$—made

by J. L. Sammis and dried at 120° C; copper isovalerianate—$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—CH_2—COO\right)_2Cu$—made from the corresponding acid, b. p. 173–175° C, not entirely free from potassium sulphate; copper acetoacetic ester—$(CH_3—CO—CH—COO.C_2H_5)_2Cu$— of Schuchardt's manufacture.

Replacement of Silver by Copper

Silver abietate, citrate, tartrate and succinate were similarly prepared, but not used to any extent as yet in this investigation. They all dissolved in pyridine and silvered metallic copper—the coating of silver finally becoming gray. In time, the copper was completely disintegrated; the succinate solution in pyridine became almost black, while the others turned green. The experiments ran for several weeks. These preliminary trials suggest that silver salts in solution will be found to give results very much like those of copper salts.

Solubility of Copper Salts

Thirty-four representative organic liquids were made as pure and anhydrous as possible and the solubility of the above copper salts determined in them. The results are summarized in Table I. In no case was the solubility more than approximately 5 percent, with the exception of many of the copper acetoacetic ester solutions. In most cases, only small amounts of the copper salts could be dissolved, but always enough to give the solutions a good green or blue color. All solutions were made as concentrated as possible, before replacement was attempted.

TABLE I—SOLUBILITY OF COPPER SALTS

(A stands for soluble; B for slightly soluble; C for insoluble; D chemical decomposition sets in)

	Camphorate	Cinnamate	Margarate	Anisate	Phthalate	Abietate	Laurate	Palmitate	Capronate	Isovalerianate	Acetoacetic ester
Carbon bisulphide	C	C	A	C	C	A	A	B	B	C	A
Toluol	C	C	A	C	C	A	A	A	A	C	A
Carbon tetrachloride	C	C	A	C	C	C	A	A	B	C	A
Chloroform	C	C	A	C	C	A	A	A	B	C	A
Ethyl acetate	C	C	C	C	C	A	B	C	B	C	A
Lactic acid	C	C	C	A	C	A	C	C	C	C	A
Acetone	C	C	C	C	C	A	A	C	A	C	A
Nitrobenzene	C	C	A	A	C	A	C	C	C	C	A
Amyl nitrate	C	C	A	A	C	D	C	A	A	B	A
Ethyl alcohol	C	B	C	C	C	C	C	C	C	C	A
Turpentine	C	C	A	C	C	A	B	B	A	C	B
Phosphorus sulpho-chloride	C	C	C	C	C	D	C	A	A	C	A
Benzol	C	C	A	C	C	A	A	B	A	C	A
Xylol	C	C	A	C	C	A	A	A	A	C	A
Pyridine	C	A	A	C	C	C	C	C	C	C	A
Cottonseed oil	C	C	A	A	C	C	C	C	C	C	B
Paraffine (fused)	C	C	A	C	C	A	B	C	B	C	B
Ether	C	C	C	C	C	A	B	C	B	C	B

TABLE 1—(*Continued*)

	Camphorate	Cinnamate	Margarate	Anisate	Phthalate	Abietate	Laurate	Palmitate	Capronate	Isovalerianate	Acetoacetic ester
Methyl acetate	C	A	A	A	B	A	A	A	A	C	A
Phosphorus trichloride	D	—	—	—	—	—	—	—	—	—	—
Ethyl sulphocyanate	A	A	A	A	C	A	A	A	A	—	A
Ethylene dibromide	C	C	C	C	C	C	A	C	C	—	C
Phenyl isocyanate	C	C	C	C	C	A	—	B	A	C	A
Acetaldehyde	C	A	—	A	C	D	A	D	D	—	D
Phenyl mustard oil	C	D	C	D	C	C	C	C	B	C	A
Pentane	C	C	A	C	C	A	C	A	A	B	A
Benzaldehyde	A	C	C	A	B	C	A	C	A	C	A
Formaldehyde (40 percent aqueous solution)	C	A	A	C	C	A	C	A	A	C	A
Ethyl benzoate	C	C	A	C	C	A	A	A	A	C	A
Amyl alcohol	C	A	A	A	B	A	A	A	A	B	A
Oleic acid	B	C	C	B	C	C	A	C	B	C	A
Acetonitrile	C	C	A	C	D	D	D	B	D	C	D
Kerosene	C	D	D	D							
Benzoyl chloride	D										

(Carbon tetrachloride dissolves copper margarate only while hot.)

Conductance of Solvents

The conductance of the pure solvent and of the concentrated solution was determined in each case. This was done by the Kohlrausch bridge method; using a resistance box of one hundred thousand ohms. Ten of the seventeen solvents measured and used had less conductance than could be measured by the apparatus. This meant a conductance of less than 2×10^{-10}. When the copper salts were dissolved in the solvents, it was not possible to predict how the conductance would be affected. In a few instances it was decreased, though the majority of cases showed a very slight increase. The conductance of all the solvents used in the following experiments is shown in Table 2. The figures indicate reciprocal ohms.

TABLE 2

Conductance of the pure solvents

Solvents	Conductance	Temperature
Oleic acid	Less than 2×10^{-10}	15°
Acetaldehyde	552×10^{-8}	20.5°
Benzaldehyde	35×10^{-8}	19.5°
Ethyl alcohol	14×10^{-7}	19.5°
Amyl alcohol	44×10^{-8}	20°
Pyridine	43×10^{-7}	21°
Acetone	10×10^{-7}	19°
Acetonitrile	71×10^{-7}	20.5°
Nitrobenzene	Less than 2×10^{-10}	20°
Carbon tetrachloride	"	20.5°
Carbon bisulphide	"	20.5°
Toluol	"	20°
Pentane	"	19.5°
Ethyl benzoate	"	19°
Ethylene dibromide	"	19°
Ether	"	20.5°
Pinene	"	23°

Copper Replacement Experiments

The method of procedure in these experiments was as follows. The saturated solution of a copper salt in one of these solvents was placed in test tubes and in each tube was

also put a small piece of carefully cleaned chemically pure metal, usually in the form of foil. The cleaning was accomplished by scouring with emery paper and then scraping bright and smooth with a steel tool. The test tubes were allowed to stand for several days and observed from time to time. Some of the experiments were conducted in oil-baths, heated to 75° C or over, and while results were generally hastened in this manner, they were practically the same as those obtained at room temperature. Most of the experiments were run for several days; but often copper deposition took place noticeably within ten minutes of the time metal and solution were brought together. The conductance of the solutions was determined at about 20° C. Data as to conductance, temperature and time will be found in Table 12. The detailed observations made in connection with each experiment follow.

Oleic Acid as Solvent

Copper cinnamate. Lead and bismuth were coppered.

Copper acetoacetic ester. Very dark green solution. Lead, zinc, bismuth and cobalt were coppered. The solution containing the mercury lightened in color a very little.

Copper palmitate. Green solution. Lead, bismuth and tin were coppered. The solutions containing lead and tin became dark yellow.

Copper abietate. Green solution. Zinc, lead and bismuth were coppered. The solutions containing zinc, lead and tin became yellow, bismuth and cobalt slightly yellow.

Copper margarate. Light green solution. Lead and zinc were coppered. The solution containing cobalt became darker, lead yellowish-green and tin yellow.

Copper anisate. Lead, zinc, tin and magnesium were coppered. On heating these solutions, they changed from a clear, dark green to a clear, light brown. On further heating, they became opaque and metallic copper separated out. In general, all oleic acid solutions behaved in a similar manner.

Copper phthalate. Lead, zinc, bismuth and magnesium were coppered.

Copper camphorate. Lead, bismuth and zinc were coppered.

Copper laurate. Bright green solution. Zinc, lead and bismuth were coppered. The solution containing cobalt became greenish-yellow, lead a trifle yellow, and mercury, zinc and tin olive green.

Copper capronate. Green solution. Zinc, lead and bismuth were coppered. The solution containing zinc became lighter, lead yellow, tin a little deeper green and cobalt a very little deeper green.

Copper isovalerianate. Light green solution, as only a very little of the salt could be dissolved. Zinc, lead and bismuth were coppered. The solution containing cobalt became a more pronounced green, zinc olive green, lead light yellow and magnesium greenish-yellow. Both cobalt and magnesium had a loosely adhering coat of brownish-black material.

Benzaldehyde as Solvent

Copper camphorate. Green solution. Cobalt, iron, zinc, lead, bismuth and tin were coppered. The solution containing cobalt became dark brown, silver darker green, mercury a trifle more yellow, aluminum light green and solid, bismuth light green, antimony more olive green, tin straw yellow, nickel solid. Magnesium was entirely disintegrated.

Copper phthalate. Light green solution. Cobalt, bismuth and lead were coppered. The solutions containing mercury, lead, zinc, bismuth, antimony, tin, magnesium and nickel became yellow, cobalt yellowish-brown, iron brownish-black. The iron was coated with a soft black substance.

Copper cinnamate. Green solution. Cobalt, zinc, magnesium, lead, bismuth, tin and antimony were coppered. The solution containing nickel became slightly yellowish, cobalt light brown, mercury light green, lead yellowish-green, aluminum and magnesium olive green, bismuth brown, antimony light greenish-yellow, tin straw yellow, and cobalt, mercury and zinc solid. A duplicate was run in the case of

antimony for eleven days, at 75° C. The metal was again coppered.

Copper abietate. Green solution. Cobalt, iron, zinc, lead, bismuth, tin and magnesium were coppered. The solution containing iron became slightly yellowish, lead still more yellow, zinc dark yellow, cobalt reddish-brown, and bismuth, tin and magnesium light yellow.

Copper margarate. Green solution. Cobalt, iron, lead, tin, aluminum, bismuth, magnesium and antimony were coppered. The solution containing nickel became slightly more yellow, cobalt and iron red, mercury yellowish-green, and zinc, lead, aluminum, bismuth, tin and magnesium yellow. A duplicate was successfully run in the case of antimony for eleven days at 75° C.

Copper anisate. Green solution. Aluminum, cobalt, zinc, iron, lead, bismuth, tin and magnesium were coppered. Magnesium was almost entirely replaced by copper. The solution containing nickel became slightly more yellow, silver and mercury a lighter green, cobalt purplish-black, iron brownish-red, and zinc, lead, bismuth, tin and magnesium yellow.

Copper palmitate. Green solution. Cobalt, zinc, iron, lead, aluminum, bismuth, tin and magnesium were coppered. The solution containing tin became slightly more yellow, cobalt and iron red, mercury greenish-yellow, and zinc, lead, bismuth, and magnesium yellow. Magnesium was almost entirely replaced by copper.

Copper isovalerianate. Light green solution. Cobalt, lead, bismuth and nickel were coppered. The solution containing iron became reddish-brown, nickel greenish-yellow, bismuth and tin light yellow, and cobalt, zinc, lead, antimony and magnesium yellow. Zinc was covered with a soft black deposit and iron with a similar gray one. Magnesium was completely disintegrated and a yellowish-white solid left. A successful duplicate was run in the case of nickel for eleven days at 75° C.

Copper acetoacetic ester. Deep blue-green solution.

Cobalt, zinc, lead, bismuth, tin and magnesium were coppered. The solution containing cobalt became a deep red, zinc reddish-brown, iron deep green, magnesium brown, and lead, tin, nickel and antimony olive green, and mercury solid. The lead and zinc tubes showed a gray precipitate and bismuth a white one.

Carbon Tetrachloride as Solvent

Copper margarate. Iron was coppered. The solution was a clear green as long as the temperature was 50° C or over. Below 50° C, the liquid separated into two layers—a clear colorless lower layer of pure solvent and a cloudy, light green upper layer, containing the salt.

Copper palmitate. No replacement. Two layers; the blue salt all came to the top.

Copper acetoacetic ester. Zinc, lead, tin, magnesium, iron and silver were coppered. In the solutions containing cobalt, silver, mercury, lead, aluminum, bismuth, antimony, tin, magnesium and nickel a whitish or greenish solid separated out. The solution containing iron became red, and zinc light brown. The silver was coated with a light gray deposit, beneath which was a little red copper on a dark background.

Copper capronate. Light blue solution. Zinc was coppered. The solution containing lead became greenish-yellow, and cobalt, mercury, zinc, aluminum and tin colorless.

Carbon Bisulphide as Solvent

Copper margarate. Nothing whatever happened.

Copper abietate. Deep green solution. Lead was coppered in the first trial, but could not be duplicated in two later attempts—one of them continued for eleven days at 75° C. The solution in all three attempts became greenish-yellow.

Copper acetoacetic ester. Brownish-red solution. The metals were all coated with an iridescent tarnish. The color of the solutions and the brown deposit on the bottom of the tubes would seem to indicate a disintegration of the copper salt and the presence of free copper.

Copper laurate. No replacement. Every solution, except the one containing antimony, had a blue solid substance separated out and floating on the top. The laurate itself is deep green.

Copper palmitate. Light green solution. No replacement. Silver, bismuth and lead were tarnished. The solution containing zinc was a trifle lighter.

Nitrobenzene as Solvent

Copper acetoacetic ester. Lead and aluminum were coppered.

Copper palmitate. Only a very little of the salt would dissolve, even when heated. The solution containing the lead became slightly more yellow.

Copper anisate. Green solution. Lead and zinc were coppered. The solution containing cobalt became blue. The silver looked as though it had been oxidized.

Pyridine as Solvent

Copper cinnamate. Lead and zinc were coppered. The salt appeared to form an addition product with the pyridine.

Copper anisate. Green solution. Silver, lead, bismuth and magnesium were coppered. The piece of silver was entirely disintegrated.

Copper phthalate. Light blue solution. The solution containing zinc became straw yellow, mercury and cobalt dark green, lead and silver light green, and aluminum, bismuth and antimony bluish-green. Silver was tarnished and zinc corroded.

Copper palmitate. Deep blue solution. Aluminum was coppered. The solution containing mercury became some lighter, silver green, lead lighter, aluminum brownish-yellow, bismuth deeper blue, magnesium yellow, and cobalt, iron and tin indigo blue. The lead, tin and nickel tubes contained a brown deposit, aluminum gray, and magnesium brownish-gray. There was a gray deposit on the silver. Magnesium was partly disintegrated.

Copper acetoacetic ester. Deep green solution. Zinc and lead were coppered. All solutions became opaque. The solution containing zinc showed a yellow precipitate, lead a light yellow, nickel a grayish-brown, and mercury and bismuth a brown. There was a grayish-yellow deposit on the silver.

Ethyl Benzoate as Solvent

Copper cinnamate. Blue-green solution. Cobalt, zinc, lead and magnesium were coppered. The solution containing cobalt became blue, and lead and magnesium colorless.

Copper abietate. Deep green solution. Zinc, lead and magnesium were coppered. The solution containing zinc became yellow, nickel slightly more yellow, and lead and magnesium brownish-yellow.

Copper palmitate. Deep green solution. Zinc, lead, bismuth, tin and magnesium were coppered. The solution containing mercury became a trifle lighter, cobalt indigo blue, zinc olive green, bismuth lighter, and lead and magnesium colorless. The bismuth tube contained a blue precipitate.

Copper acetoacetic ester. Deep green solution. Cobalt, zinc, lead and magnesium were coppered. The solution containing iron became much darker, lead light yellow, zinc olive green, magnesium yellowish-green, mercury and cobalt light green, silver and tin light blue, bismuth and antimony a trifle lighter. A light blue precipitate formed in the tubes containing mercury, cobalt, silver, tin, zinc, bismuth, antimony and magnesium.

Toluol as Solvent

Copper abietate. Green solution. The solution containing lead became slightly yellowish and the metal tarnished.

Copper margarate. Green solution. No replacement. The solution containing cobalt became slightly yellow, and and iron yellowish-green.

Copper acetoacetic ester. Deep green solution. Zinc was coppered. The solution containing lead became slightly yellow, nickel brown, and antimony grayish-yellow.

Copper palmitate. No replacement. The solution containing lead became more green. Zinc was corroded.

Amyl Alcohol as Solvent

Copper abietate. Green solution. Lead and aluminum were coppered. A successful duplicate was run in the case of the aluminum for fifteen days at 75° C, but the metal was coppered only on an edge that protruded from the solution. This was no doubt due to the solubility of copper in the alcohol. A yellowish-green precipitate was formed. The other metals gave the following results: cobalt, magnesium and nickel gave yellowish solutions; lead and aluminum yellowish-brown solutions and precipitates; cobalt, nickel, magnesium, antimony and bismuth tubes contained brown, needle-shaped crystals, which were translucent and non-malleable.

Copper palmitate. Bluish-green solution. Silver was coppered and this was later duplicated. The solution containing zinc became slightly yellowish and magnesium yellowish-green, iron more blue—with a light colored precipitate, lead greenish-yellow—with a light colored precipitate. Bismuth was covered with an iridescent tarnish. There was a brownish deposit in the solutions containing magnesium, nickel, tin, antimony, aluminum, zinc, silver and cobalt.

Copper capronate. Green solution. Aluminum and lead were coppered. In a duplicate run in the case of aluminum for fifteen days at 75° C, the metal was coppered as before and a black precipitate formed. The solution containing magnesium became very light blue, lead greenish-yellow, cobalt, mercury, zinc, bismuth, tin and aluminum dark brown, and nickel, antimony, iron and silver yellowish-brown. Bismuth showed an iridescent tarnish. There was a gray deposit on the silver and magnesium.

Copper acetoacetic ester. Green solution. Aluminum and silver were coppered—the latter also in a duplicate. The solution containing aluminum became dark greenish-yellow, lead yellowish-green, antimony greenish-yellow. The

mercury and zinc tubes contained a dark brown precipitate, cobalt, iron, bismuth, magnesium and nickel a green, lead a white, and antimony a brown. Bismuth had an iridescent tarnish and there was a grayish-black deposit in the solution containing magnesium.

Ethyl Alcohol as Solvent

Copper acetoacetic ester. Clear dark green solution. Zinc, lead and aluminum were coppered. The solution containing zinc became yellow, cobalt and bismuth lighter green—also a green precipitate, silver and nickel light yellow—a brown precipitate, mercury light green—a green precipitate, aluminum light brown, antimony greenish-yellow—a dark green precipitate, tin colorless—a white precipitate—a gray coating on the metal, magnesium yellowish-green—a dirty white coating on the metal, lead grayish-yellow and a precipitate of the same color.

Pinene as Solvent

Copper palmitate. Green solution. Cobalt was coppered. The solution containing antimony became a trifle lighter, mercury yellow, magnesium, tin and cobalt pale green, lead and zinc brownish-yellow—with yellow precipitates, iron yellowish-brown—the metal was corroded. The silver was tarnished and the magnesium looked brassy. Zinc and lead had a black deposit on the metal, and bismuth a gray.

Copper abietate. Very light green solution. Zinc was coppered. The solution containing iron became a little lighter, and the silver and bismuth yellow.

Copper acetoacetic ester. Deep green solution. Nothing whatever happened.

Acetonitrile as Solvent

Copper acetoacetic ester. Light green solution. No replacement. The solution containing cobalt became more

yellow, zinc and lead still more yellow, nickel more yellow still, silver, mercury, aluminum and tin greenish-yellow, iron and antimony yellowish-green, bismuth yellowish-green—a precipitate of same color, magnesium almost colorless—a gray precipitate—metal completely dissolved, nickel a yellowish-gray precipitate and aluminum a yellowish-brown.

Copper anisate. Very light green solution. No replacement. The solution containing cobalt became brownish-yellow, iron and antimony yellow, and mercury, zinc, lead, aluminum, tin, magnesium and nickel colorless; zinc, aluminum and magnesium a white precipitate, antimony a yellow and bismuth a light colored one. Aluminum and magnesium were both corroded.

Copper capronate. Green solution. No replacement. The solution containing tin became a deeper green, cobalt, mercury and aluminum light yellow, nickel and zinc greenish-yellow, antimony deep yellow, magnesium light blue, lead colorless and an iridescent tarnish formed on the metal. Bismuth showed a similar tarnish. Aluminum and magnesium were corroded.

Ether as Solvent

Copper abietate. Very light green solution. No replacement. The solution containing mercury became a little more yellow.

Copper acetoacetic ester. Light green solution. No replacement. The solution containing mercury became a deeper green, aluminum yellow, antimony greenish-yellow, and cobalt, zinc, tin and magnesium slightly yellowish.

Pentane as Solvent

Copper capronate. Light green solution. No replacement. The solution containing lead became light yellow, mercury and zinc colorless.

Copper acetoacetic ester. Nothing whatever happened.

Acetaldehyde as Solvent

Copper cinnamate. Zinc, iron, aluminum and lead were coppered.

Copper acetoacetic ester. Light blue-green solution. Zinc and iron were coppered. The solution containing zinc became a little yellow, iron deeper yellow, cobalt slightly more blue—metal corroded, aluminum colorless—a rough black deposit on the metal, bismuth a light grayish-white precipitate. Magnesium was corroded.

Copper palmitate. Light blue solution. Cobalt, zinc and iron were coppered. The solution containing cobalt became dark brown, iron light brown, zinc light yellow, lead colorless, magnesium almost colorless, and silver, mercury, tin and nickel slightly lighter. The lead and bismuth tubes contained a gray deposit.

Acetone as Solvent

Copper abietate. Light green solution. No replacement. The solution containing magnesium became slightly yellowish, and mercury, antimony and aluminum slightly turbid.

Copper acetoacetic ester. Deep green solution. Magnesium was coppered—under a grayish-black deposit. The solution containing magnesium became greenish-blue, cobalt and bismuth slightly yellowish, silver, mercury, iron, lead and nickel cloudy. Cobalt, lead, bismuth and antimony were tarnished. Aluminum had a black coating. There was a brown deposit on the antimony and cobalt tubes. This was dissolved in nitric acid to a green solution, evaporated to dryness and the nitrate decomposed by heat. Brown copper oxide was left.

Copper capronate. Light blue solution. No replacement. The solution containing antimony became greenish-blue, zinc, lead and magnesium lighter, iron slightly yellowish, aluminum a light colored precipitate. Lead had a grayish-yellow coating and bismuth a yellowish tarnish.

Ethylene Dibromide as Solvent

Copper palmitate. Deep blue solution. Zinc and lead were coppered. The solution containing nickel became

bluish-green, zinc colorless—a yellow precipitate, lead yellow—a whitish precipitate. The solution containing silver contained a grayish deposit, iron a dark gray, aluminum a black. Cobalt had a yellow deposit on the metal, and antimony and magnesium each a yellowish-brown coating. The solution containing antimony and magnesium became dark yellow in both cases and a dark brown precipitate formed on the tubes at the top of the liquids. The metal bismuth was darkened.

Copper acetoacetic ester. Deep green solution. Zinc was coppered. The solution containing nickel became blue-green, silver and bismuth lightened a little, cobalt brownish-black, zinc yellow, lead yellow-brown—a precipitate of the same color and a black deposit, aluminum dirty green—a precipitate of the same color and a gray deposit, antimony dark red and there was a thick, dark brown, gummy mass on the metal and tube. The magnesium tube showed a dirty brown precipitate and solution, and a dark deposit. The silver tube contained a brownish-yellow deposit and iron a gray one.

Copper anisate. Deep blue solution. Zinc and lead were coppered. The solution containing zinc became colorless, cobalt yellow, bismuth green, antimony light green, silver lighter—a yellowish-brown deposit, mercury yellow—a thick, brown paste on the tube, iron red—a blackish-brown deposit, lead colorless—a white precipitate, aluminum very light yellow—a grayish-black deposit, tin yellow—a thick, brown substance on the metal, which was very soft, magnesium dirty greenish-yellow—a gray deposit, nickel yellow—a soft yellow deposit.

Three solutions in contact with metallic mercury were observed for twenty-two months, to see if color changes could be noticed. (1) Copper acetoacetic ester in amyl alcohol. The dark green solution became grass-green and a precipitate of the same color separated out. (2) Copper acetoacetic ester in acetonitrile. The green solution became brown and a slight green precipitate formed. (3) Copper phthalate in pyridine. The blue solution became light green. As blank

solutions without mercury showed none of these changes, it would appear that some reaction had taken place in each case.

There now follows a series of experiments in which the time of exposure was much longer and the temperature higher. They were all conducted in sealed tubes. The solvents were specially prepared as follows: (1) Amyl alcohol was dried over copper sulphate and twice fractionated. The fraction distilling between 130° and 131° C was used. Its conductance was 18×10^{-10}. (2) Ethyl benzoate was twice distilled. B. P. was 213° C and conductance was less than 2×10^{-8} at 17.6° C. (3) Pyridine was distilled from calcium chloride at 115° C, after long standing. Its conductance was 25×10^{-8} at 17.6° C. (4) Carbon tetrachloride was twice distilled. B. p. was 77° C. Its conductance was less than 2×10^{-10} at 19° C.

The data of Tables 3–11 show that higher temperature and longer duration of time simply influence the quantitative side of the experiments. The brassy appearance observed in some cases was interesting and indicates the formation of copper alloys. This effect was observed with all the metals used except magnesium and mercury, the first of which was usually heavily coppered, while the mercury would dissolve the copper.

All replacement results secured with copper salts in solution have been collected in Table 12. All the metals were used in all the experiments, with the exception of cadmium, which was tried in only nine cases of the sixty-nine. Where metallic copper was thrown out, it is indicated in the table by a cross (X). A good many experiments showed no copper, but evidences of chemical action were plain—such as a change in color of the solution or the formation of a precipitate. These cases are marked in the table with a circle (O). The most plausible explanation of these "indicated" replacements is that the solvent or solution or both have slight solvent properties toward copper or the other metal present. This was actually found to be the case in a number of instances. When mercury was used, any replaced copper

TABLE 3

Copper Acetoacetic Ester in Carbon Tetrachloride

Conductance less than 2×10^{-10} — Very deep green solution

Metal	Time	Temp.	Solution change	Metal change
Ag	7 days	20° C	Lighter green—cloudy	Faintly coppered and black
Zn	7 days	20° C	Lighter green—cloudy	Brownish-black
Mg	7 days	20° C	Lighter green—cloudy	Dark copper
Pb	7 days	20° C	Lighter green—cloudy	Coppered and black. Best
Fe	7 days	20° C	Yellow-brown—cloudy	Darkened a little—brownish
Hg	7 days	20° C	Lighter green—cloudy	
Ni	7 days	20° C	Lighter green—cloudy	
Al	7 days	20° C	Lighter green—cloudy	Grayish in places
Sn	7 days	20° C		Blackened above solution
Hg	25 days	75° C	Colorless—yellow ppt.	
Ni	25 days	75° C	Color'ess—yellow ppt.	Dulled
Al	25 days	75° C	Colorless—yellow ppt.	Gray
Sn	25 days	75° C	Colorless—yellow ppt.	Grayish-black

After 25 days at 75° C, a blank solution became colorless and a very light yellow precipitate settled out. This was also true of all the solutions with metals.

Carbon tetrachloride had no action on copper, save to make it dull, where it was bright to begin with.

TABLE 4

Copper Abietate in Amyl Alcohol

Conductance—30×10^{-8} Grass-green solution

Metal	Time	Temp.	Solution change	Metal change
Cd	20 days	20° C	Yellow	Coppered
Mg	20 days	20° C	Yellow	Coppered
Pb	20 days	20° C	Color unchanged—cloudy	Coppered
Zn	20 days	20° C	Color slightly yellowish	Darkened
Fe	20 days	20° C	Unchanged	Unchanged
Ni	20 days	20° C	Unchanged	Unchanged
Sb	20 days	20° C	Unchanged	Unchanged
Co	20 days	20° C	Unchanged	Unchanged
Bi	20 days	20° C	Unchanged	Unchanged
Sn	20 days	20° C	Unchanged	Unchanged
Hg	20 days	20° C	Unchanged	Unchanged
Al	20 days	20° C	Unchanged	Unchanged
Ag	20 days	20° C	Unchanged	Unchanged
Zn	25 days	75° C	Dark yellow—ppt. same	Darkened
Fe	25 days	75° C	Dark yellow—ppt. same	Brassy
Ni	25 days	75° C	Dark yellow—ppt. same	Brassy
Sb	25 days	75° C	Dark yellow—ppt. same	Brassy
Co	25 days	75° C	Tube broke	Brassy
Bi	25 days	75° C	Tube broke	Brassy
Sn	25 days	75° C	Dark yellow—ppt. same	Brassy
Hg	25 days	75° C	Dark yellow—ppt. same	
Al	25 days	75° C	Dark yellow—ppt. same	Brassy
Ag	25 days	75° C	Dark yellow—ppt. same	Brassy

After 25 days at 75° C, a blank solution became dark yellow and a precipitate of the same color separate out.

After 15 hours at 95° C, silver was very yellow, suggesting a copper alloy. Zinc became brassy.

Copper in amyl alcohol gave a slightly greenish-yellow solution. This became yellow and a precipitate of the same color separated after 25 days at 75° C.

TABLE 5

Copper Palmitate in Amyl Alcohol

Conductance—73 × 10^{-8}. Light blue solution—later light yellow

Metal	Time	Temp.	Solution change	Metal change
Mg	15 days	20° C	Unchanged	Grayish-black
Zn	15 days	20° C	Unchanged	Brassy
Cd	15 days	20° C	Colorless—white ppt.	Coppered and black
Pb	15 days	20° C	Colorless—white ppt.	Coppered and black
Ag	15 days	20° C	Unchanged	Brassy
Hg	15 days	20° C	Unchanged	
Sb	15 days	20° C	Unchanged	Unchanged
Ni	15 days	20° C	Unchanged	Unchanged
Al	15 days	20° C	Unchanged	Unchanged
Bi	15 days	20° C	Unchanged	Unchanged
Fe	15 days	20° C	Unchanged	Unchanged
Co	15 days	20° C	Unchanged	Unchanged
Sn	15 days	20° C	Unchanged	Unchanged
Ag	25 days	75° C	Yellow—ppt. same	Brassy
Hg	25 days	75° C	Yellow—ppt. same	
Sb	25 days	75° C	Yellow—ppt. same	Brassy
Ni	25 days	75° C	Yellow—ppt. same	Brassy
Al	25 days	75° C	Yellow—ppt. same	Brassy
Bi	25 days	75° C	Yellow—ppt. same	Brassy
Fe	25 days	75° C	Yellow—ppt. same	Brassy
Co	25 days	75° C	Yellow—ppt. same	Brassy
Sn	25 days	75° C	Yellow—ppt. same	Brassy

After 25 days at 75° C, a blank solution became colorless and a brownish-yellow precipitate formed. After 15 hours more at 95° C, the solution was yellow and the precipitate the same as before.

After 15 hours at 95° C, the brassy appearance disappeared from the nickel and antimony. Silver became *very* yellow.

TABLE 6

Copper Acetoacetic Ester in Ethyl Benzoate

Conductance less than 2×10^{-10} Deep green-blue solution

Metal	Time	Temp.	Solution change	Metal change
Mg	12 days	20° C	Little greener—ppt.	Coppered
Cd	12 days	20° C	Little greener—ppt.	Coppered
Pb	12 days	20° C	Light green—ppt.	Coppered
Zn	12 days	20° C	Darker than Pb—ppt.	Coppered
Fe	12 days	20° C	Color unchanged—ppt.[1]	Blackened a little
Sn	12 days	20° C	Color unchanged—ppt.	Unchanged
Ni	12 days	20° C	Color unchanged—ppt.[1]	Unchanged
Sb	12 days	20° C	Color unchanged—ppt.[1]	Unchanged
Ag	12 days	20° C	Color unchanged—ppt.[1]	Unchanged
Al	12 days	20° C	Color unchanged—ppt.	Unchanged
Co	12 days	20° C	Color unchanged—ppt.[1]	Unchanged
Hg	12 days	20° C	Color unchanged—ppt.	
Bi	12 days	20° C	Color unchanged—ppt.[1]	Unchanged
Fe	25 days	75° C	Blue salt separated	Unchanged
Sn	25 days	75° C	Blue salt separated	Unchanged
Ni	25 days	75° C	Blue salt separated	Unchanged
Sb	25 days	75° C	Blue salt separated	Unchanged
Ag	25 days	75° C	Blue salt separated	Unchanged
Hg	25 days	75° C	Blue salt separated	
Bi	25 days	75° C	Blue salt separated	Much darkened
Al	25 days	75° C	Olive green	Unchanged
Co	25 days	75° C	Olive green	Coppered slightly

[1] One or more large, deep blue crystals separated out.

In every case there was a light blue precipitate. After 25 days at 75° C, from a blank solution there separated a blue solid. After 15 hours at 95° C, aluminum became slightly brassy.

Copper in ethyl benzoate gave a deep greenish-blue solution. After 25 days at 75° C, a precipitate formed on the tube and metal, which looked like freshly deposited copper. At the same time the solution became light green.

TABLE 7

Copper Pal. itate in Ethyl Benzoate

Conductance less than 2×10^{-10} Greenish-blue solution

Metal	Time	Temp.	Solution change	Metal change
Pb	12 days	20° C	Color unchanged—white ppt.	Coppered
Zn	12 days	20° C	Slightly greener	Coppered
Cd	12 days	20° C	Light green—white jelly	Coppered
Mg	12 days	20° C	Colorless	Coppered
Sn	12 days	20° C	Slightly yellow	Coppered
Co	12 days	20° C	Purplish-blue	Unchanged
Al	12 days	20° C	Unchanged	Unchanged
Ag	12 days	20° C	Unchanged	Unchanged
Fe	12 days	20° C	Unchanged	Unchanged
Hg	12 days	20° C	Unchanged	
Ni	12 days	20° C	Unchanged	Unchanged
Sb	12 days	20° C	Unchanged	Unchanged
Bi	12 days	20° C	Almost colorless—white gelatinous ppt.	Unchanged
Co	25 days	75° C	Deep purple	Coppered
All others	25 days	75° C	Unchanged	Unchanged

After 15 hours at 95° C, there were no further changes.

TABLE 8

Copper Cinnamate in Ethyl Benzoate

Conductance less than 2×10^{-10} — Greenish-blue solution

Metal	Time	Temp.	Solution change		Metal change
Cd	7 days	20° C	Very light green		Coppered
Mg	7 days	20° C	Almost colorless		Coppered
Pb	7 days	20° C	Colorless		Coppered
Zn	7 days	20° C	Color unchanged—white ppt.		Coppered
Sn	7 days	20° C	Unchanged		Coppered at liquid surface
Ag	7 days	20° C	Unchanged		Unchanged
Hg	7 days	20° C	Unchanged		
Al	7 days	20° C	Unchanged		Unchanged
Ni	7 days	20° C	Unchanged		Unchanged
Bi	7 days	20° C	Unchanged		Unchanged
Fe	7 days	20° C	Unchanged		Unchanged
Sb	7 days	20° C	Unchanged		Unchanged
Co	7 days	20° C	Deep blue		Unchanged
Ag	25 days	75° C	Unchanged		Unchanged
Hg	25 days	75° C	Unchanged		
Al	25 days	75° C	Unchanged		Unchanged
Ni	25 days	75° C	Unchanged		Unchanged
Bi	25 days	75° C	Unchanged		Tarnished
Sb	25 days	75° C	Unchanged		Unchanged
Co	25 days	75° C	Purplish-blue.	Light lavender ppt.	Darkened

After 15 hours at 95° C, there were no further changes.

TABLE 9

Copper Abietate in Ethyl Benzoate

Conductance less than 2×10^{-10} Very dark green solution

Metal	Time	Temp.	Solution change	Metal change
Cd	7 days	20° C	Color unchanged—ppt.	Coppered
Pb	7 days	20° C	Colorless, yellow-green ppt.	Coppered
Mg	7 days	20° C	Colorless, yellow-green ppt.	Coppered
Zn	7 days	20° C	Yellow-brown	Coppered
Ni	7 days	20° C	Unchanged	Unchanged
Ag	7 days	20° C	Unchanged	Unchanged
Sn	7 days	20° C	Unchanged	Unchanged
Fe	7 days	20° C	Unchanged	Unchanged
Bi	7 days	20° C	Unchanged	Unchanged
Last five	25 days	75° C	Unchanged	Unchanged

After 15 hours at 95° C, silver was brassy.

TABLE 10

Copper Cinnamate in Pyridine

Conductance—117×10^{-8} Deep blue solution

Metal	Time	Temp.	Solution change	Metal change
Pb	6 days	20° C	Light blue—blue ppt.	Brassy
Ag	6 days	20° C	Light green—b ue ppt.	Unchanged
Bi	6 days	20 °C	Light blue—blue ppt.	Unchanged
Al	6 days	20° C	Light blue—blue ppt.	Unchanged
Fe	6 days	20° C	Light blue—blue ppt.	Unchanged
Mg	6 days	20° C	Light green—blue ppt.	Unchanged
Sn	6 days	20° C	Light green—blue ppt.	Unchanged
Hg	6 days	20° C	Light green—blue ppt.	Unchanged
Ni	6 days	20° C	Green—blue ppt.	Unchanged
Zn	6 days	20° C	Green—blue ppt.	Unchanged
Cd	6 days	20° C	Green—blue ppt.	Unchanged
Sb	6 days	20° C	Green—blue ppt.	Unchanged
Co	6 days	20° C	Brown—blue ppt.	Unchanged
Zn	25 days	75° C	Very light yellow	Coppered
Ag	25 days	75° C	Tube broke	Unchanged
Sn	25 days	75° C	Tube broke	Unchanged
Al	25 days	75° C	Very light green—blue ppt.	Unchanged
Ni	25 days	75° C	Greenish-yellow—blue ppt.	Unchanged
Bi	25 days	75° C	Light green—blue ppt.	Unchanged
Sb	25 days	75° C	Light green—blue ppt.	Unchanged
Mg	25 days	75° C	Yellow—blue ppt.	Unchanged
Fe	25 days	75° C	Green—blue ppt.	Unchanged
Hg	25 days	75° C	Green—blue ppt.	Unchanged
Cd	25 days	75° C	Green—blue ppt.	Unchanged
Co	25 days	75° C	Brown	Unchanged

Immediately on sealing, the blank solution and also those containing silver and magnesium turned yellowish-green; mercury, nickel, lead, tin became greenish-blue; cobalt became dark lavender.

After 15 hours at 95° C, cobalt was slightly brassy.

Copper in pyridine gave an olive green solution and a blue salt crystallized out. After 25 days at 75° C, the solution became yellow and a brownish-yellow precipitate settled out on the sides of the tube. Copper itself became blackish-brown.

TABLE II

Copper Palmitate in Pyridine

Conductance—46 × 10^{-8} Blue-green solution

Metal	Time	Temp.	Solution change	Metal change
Pb	4 days	20° C	Greener	Darkened
Zn	4 days	20° C	Greener	Unchanged
Hg	4 days	20° C	Greener	Unchanged
Mg	4 days	20° C	Blue. Green ppt.	Unchanged
Ni	4 days	20° C	B uer	Unchanged
Al	4 days	20° C	Bluer	Unchanged
Sn	4 days	20° C	Deep blue	Unchanged
Ag	4 days	20° C	Unchanged	Unchanged
Cd	4 days	20° C	Unchanged	Unchanged
Bi	4 days	20° C	Unchanged	Unchanged
Fe	4 days	20° C	Unchanged	Unchanged
Sb	4 days	20° C	Unchanged	Unchanged
Co	4 days	20° C	Unchanged	Unchanged
Pb	25 days	75° C	Greenish-yellow	Coppered slightly
Zn	25 days	75° C	Tube broke	Brassy
Mg	25 days	75° C	Tube broke	Unchanged
Sn	25 days	75° C	Tube brobe	Unchanged
Hg	25 days	75° C	Green	Unchanged
Cd	25 days	75° C	Green	Unchanged
Ag	25 days	75° C	Unchanged	Unchanged
Ni	25 days	75° C	Unchanged	Unchanged
Also	Bi, Fe, Al, Sb, Co		Unchanged	Unchanged

After 15 hours at 95° C, the solution containing cadmium became dark brown and the metal was brassy in places.

was at once amalgamated, and analysis of the mercury, in representative cases, proved this. In order to be sure that "indicated" results were really effects of the metals introduced, blanks were invariably run. In 20.2 percent of all of the solutions indicated in this table, metallic copper was thrown out, while 27 percent more showed indirect evidence of replacement.

The number of cases where actual replacement occurred, as compared with the number of cases where no replacement resulted, varied when the same salt was dissolved in different solvents. The number also varied in the case of the same

TABLE 12

Copper Replacements

Copper salt	Solvent	Cond. of solvent	Cond. of solution	Days	Temp.	Co	Ag	Hg	Zn	Fe	Pb	Al	Bi	Sb	Sn	Mg	Ni	Cd
Cinnamate	Oleic acid	2×10^{-10}	2×10^{-10}	4	—	—	—	—	—	—	X	—	X	—	—	—	—	—
Acetoacetate	Oleic acid	2×10^{-10}	2×10^{-10}	3	80°	X	—	O	X	—	X	—	X	—	—	—	—	—
Palmitate	Oleic acid	2×10^{-10}	2×10^{-10}	3	80°	—	—	—	—	—	X	—	X	—	X	—	—	—
Abietate	Oleic acid	2×10^{-10}	2×10^{-10}	6	80°	O	—	—	X	—	X	—	X	—	O	—	—	—
Margarate	Oleic acid	2×10^{-10}	2×10^{-10}	3	80°	O	—	—	X	—	X	—	—	—	O	—	—	—
Anisate	Oleic acid	2×10^{-10}	2×10^{-10}	4	—	—	—	—	X	—	X	—	—	—	X	X	—	—
Phthalate	O eic acid	2×10^{-10}	2×10^{-10}	3	80°	—	—	—	X	—	X	—	X	—	—	X	—	—
Camphorate	Oleic acid	2×10^{-10}	2×10^{-10}	—	—	—	—	—	X	—	X	—	X	—	—	—	—	—
Laurate	Oleic acid	2×10^{-10}	2×10^{-10}	3	80°	O	—	O	X	—	X	—	X	—	O	—	—	—
Capronate	Oleic acid	2×10^{-10}	2×10^{-10}	3	80°	O	—	—	X	—	X	—	X	—	O	—	—	—
Isovalerianate	Oleic acid	2×10^{-10}	2×10^{-10}	3	80°	O	—	—	X	—	X	—	X	—	O	O	—	—
Camphorate	Benzaldehyde	35×10^{-6}	17×10^{-7}	3	80°	X	O	O	X	X	X	O	X	O	X	—	O	—
Cinnamate	Benzaldehyde	35×10^{-6}	49×10^{-6}	3	80°	X	—	O	X	—	X	O	X	X	X	—	O	—
Phthalate	Benzaldehyde	35×10^{-6}	42×10^{-6}	4	80°	X	—	O	O	O	X	—	X	O	O	X	O	—
Abietate	Benzaldehyde	35×10^{-6}	31×10^{-7}	4	80°	X	—	—	X	X	X	—	X	—	X	X	O	—
Margarate	Benzaldehyde	35×10^{-6}	96×10^{-6}	3	80°	X	—	O	O	X	X	X	X	X	X	X	O	—
Anisate	Benzaldehyde	35×10^{-6}	33×10^{-6}	3	80°	X	O	O	X	X	X	X	X	—	X	X	O	—
Palmitate	Benzaldehyde	35×10^{-6}	56×10^{-7}	3	80°	X	—	O	X	X	X	X	X	—	X	X	O	—
Isovalerianate	Benzaldehyde	35×10^{-6}	21×10^{-6}	4	75°	X	—	—	O	O	X	—	X	O	O	O	X	—
Acetoacetate	Beanzldehyde	35×10^{-6}	40×10^{-6}	4	75°	X	—	O	X	O	X	—	X	O	X	X	O	—

TABLE 12—(*Continued*)

Copper salt	Solvent	Cond. of solvent	Cond. of solution	Days	Temp.	Co	Ag	Hg	Zn	Fe	Pb	Al	Bi	Sb	Sn	Mg	Ni	Cd
Cinnamate	Pyridine	43×10^{-7}	20×10^{-7}	4	—	O	—	—	X	—	X	—	—	—	—	—	—	—
Anisate	Pyridine	43×10^{-7}	—	5	—	—	X	—	—	—	X	—	X	—	—	X	—	—
Phthalate	Pyridine	43×10^{-7}	95×10^{-7}	3	80°	O	O	O	O	—	O	O	O	O	—	—	—	—
Palmitate	Pyridine	43×10^{-7}	53×10^{-7}	4	75°	O	O	O	—	O	X	X	O	—	O	O	O	X
Acetoacetate	Pryidine	43×10^{-7}	73×10^{-7}	4	75°	—	O	O	X	—	X	—	O	—	—	—	O	—
Margarate	Carbon bisulphide	2×10^{-10}	2×10^{-10}	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Abietate	Carbon bisulphide	2×10^{-10}	2×10^{-10}	4	—	—	—	—	—	—	O	—	—	—	—	—	—	—
Acetoacetate	Carbon bisulphide	2×10^{-10}	2×10^{-10}	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Laurate	Carbon bisulphide	2×10^{-10}	2×10^{-10}	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Palmitate	Carbon bisulphide	2×10^{-10}	2×10^{-10}	3	—	—	—	—	O	—	—	—	—	—	—	—	—	—
Margarate	Carbon tetrachloride	2×10^{-10}	2×10^{-10}	5	—	—	—	—	—	X	—	—	—	—	—	—	—	—
Palmitate	Carbon tetrachloride	2×10^{-10}	2×10^{-10}	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Acetoacetate	Carbon tetrachloride	2×10^{-10}	2×10^{-10}	4	80°	—	X	—	X	X	X	—	—	—	X	X	—	—
Capronate	Carbon tetrachloride	2×10^{-10}	2×10^{-10}	4	—	O	—	O	X	—	O	O	—	—	O	—	—	—
Anisate	Nitrobenzene	2×10^{-10}	11×10^{-8}	4	80°	O	—	—	X	—	X	—	—	—	—	—	—	—
Acetoacetate	Nitrobenzene	2×10^{-10}	94×10^{-8}	4	75°	—	—	—	—	—	X	X	—	—	—	—	—	—
Palmitate	Nitrobenzene	2×10^{-10}	2×10^{-10}	3	75°	—	—	—	—	—	O	—	—	—	—	—	—	—
Abietate	Amyl alcohol	44×10^{-8}	51×10^{-8}	3	75°	O	O	O	O	O	X	X	O	O	O	X	O	X
Palmitate	Amyl alcohol	44×10^{-8}	13×10^{-7}	3	75°	—	X	—	X	O	X	—	—	—	—	O	—	X
Capronate	Amyl alcohol	44×10^{-8}	58×10^{-8}	3	75°	O	O	O	O	O	X	X	O	O	O	O	O	—
Acetoacetate	Amyl alcohol	44×10^{-8}	62×10^{-8}	3	75°	—	X	O	O	—	O	X	—	O	—	O	—	—

TABLE 12—(*Continued*)

Copper Salt	Solvent	Cond. of solvent	Cond. of solution	Days	Temp.	Co	Ag	Hg	Zn	Fe	Pb	Al	Bi	Sb	Sn	Mg	Ni	Cd
Abietate	Toluol	2×10^{-10}	2×10^{-10}	3	75°	—	—	—	—	—	O	—	—	—	—	—	—	—
Margarate	Toluol	2×10^{-10}	2×10^{-10}	3	75°	O	—	—	—	O	—	—	—	—	—	—	—	—
Acetoacetate	Toluol	2×10^{-10}	2×10^{-10}	3	75°	—	—	—	X	—	O	—	—	O	—	—	O	—
Palmitate	Toluol	2×10^{-10}	2×10^{-10}	3	75°	—	—	—	—	—	O	—	—	—	—	—	—	—
Cinnamate	Ethyl benzoate	2×10^{-10}	2×10^{-10}	4	75°	X	—	—	X	—	X	—	—	—	X	X	—	X
Abietate	Ethyl benzoate	2×10^{-10}	2×10^{-10}	4	75°	—	O	—	X	—	X	—	—	—	—	X	—	X
Palmitate	Ethyl benzoate	2×10^{-10}	$2 = 10^{-10}$	4	75°	X	—	O	X	—	X	—	X	—	X	X	O	X
Acetoacetate	Ethyl benzoate	2×10^{-10}	2×10^{-10}	4	75°	X	O	O	X	O	X	O	O	O	O	X	—	X
Palmitate	Pinene	2×10^{-10}	2×10^{-10}	7	75°	X	—	O	O	O	O	—	O	O	O	O	—	—
Acetoacetate	Pinene	2×10^{-10}	2×10^{-10}	3	75°	—	—	—	—	—	—	—	—	—	—	—	—	—
Abietate	Pinene	2×10^{-10}	2×10^{-10}	3	75°	—	O	—	X	O	—	—	O	—	—	—	—	—
Acetoacetate	Acetonitrile	71×10^{-7}	27×10^{-6}	3	75°	O	O	O	O	O	O	O	O	O	O	O	O	—
Anisate	Acetonitrile	71×10^{-7}	40×10^{-6}	3	75°	O	—	O	O	O	O	O	O	O	O	O	O	—
Capronate	Acetonitrile	71×10^{-7}	—	3	75°	O	—	O	O	—	O	O	—	O	O	O	O	—
Acetoacetate	Ether	2×10^{-10}	2×10^{-10}	3	—	O	—	O	O	—	—	O	—	O	O	O	—	—
Abietate	Ether	2×10^{-10}	2×10^{-10}	3	—	—	—	O	—	—	—	—	—	—	—	—	—	—

TABLE 12—(*Continued*)

Copper salt	Solvent	Cond. of solvent	Cond. of solution	Days	Temp.	Co	Ag	Hg	Zn	Fe	Pb	Al	Bi	Sb	Sn	Mg	Ni	Cd
Palmitate	Ethylene dibromide	2×10^{-10}	2×10^{-10}	4	75°	O	O	O	X	O	X	O	—	O	O	O	O	—
Acetoacetate	Ethylene dibromide	2×10^{-10}	2×10^{-10}	4	75°	O	O	—	X	O	O	O	O	O	—	O	O	—
Anisate	Ethylene dibromide	2×10^{-10}	2×10^{-10}	4	75°	O	O	O	X	O	X	O	O	O	O	O	O	—
Acetoacetate	Ethyl alcohol	14×10^{-7}	12×10^{-16}	3	75°	O	O	O	X	—	X	X	O	O	O	O	O	—
Abietate	Acetone	10×10^{-7}	29×10^{-7}	4	—	—	—	—	—	—	—	—	—	—	—	O	—	—
Acetoacetate	Acetone	10×10^{-7}	12×10^{-7}	4	—	O	—	—	O	—	—	O	O	—	—	X	—	—
Capronate	Acetone	10×10^{-7}	66×10^{-8}	4	—	—	—	—	O	O	O	—	O	O	—	O	—	—
Cinnamate	Acetaldehyde	552×10^{-8}	557×10^{-8}	3	—	—	—	—	X	X	X	X	—	—	—	—	—	—
Acetoacetate	Acetaldehyde	552×10^{-8}	639×10^{-8}	4	—	O	—	—	X	X	—	O	O	—	—	—	—	—
Palmitate	Acetaldehyde	552×10^{-8}	—	4	—	X	O	O	X	X	O	—	O	—	O	O	O	—
Acetoacetate	Pentane	2×10^{-10}	2×10^{-10}	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Capronate	Pentane	2×10^{-10}	2×10^{-10}	3	—	—	—	O	O	—	O	—	—	—	—	—	—	—

solvent when different salts were dissolved in it. And again the number of cases in which action occurred varied when the same metal was used to replace copper in different solutions. For the purpose of comparing the various solvents, as to the ratio of the actual number of replacements to non-replacements, Table 13 was compiled. The various salts are similarly compared in Table 14 and the various metals in Table 15. This comparison can only be approximate, since the salts were not all used in the same number of experiments, nor were the solvents. The ratios do indicate roughly which combinations of salt and solvent might be expected to give the largest percentage of instances of copper replacement. Table 15 is more significant, since all the metals but cadmium were given an equal opportunity to replace copper.

TABLE 13

Copper Replacements Secured in the Various Solvents

Solvent	Actual replacements Percent	Actual and indicated replacements Percent	Experiments performed
Oleic acid	25.7	34.8	132
Benzaldehyde	52.7	80.5	108
Pyridine	16.6	53.5	62
Carbon bisulphide	0.0	3.3	60
Ethyl benzoate	42.5	61.5	52
Amyl alcohol	20.1	75.0	50
Carbon tetrachloride	16.6	27.1	49
Toluol	2.1	16.6	48
Acetaldehyde	25.0	52.8	36
Ethylene dibromide	13.9	91.6	36
Nitrobenzene	11.1	16.6	36
Pinene	5.5	36.1	36
Acetone	2.8	30.5	36
Acetonitrile	0.0	89.0	36
Ether	0.0	33.3	24
Pentane	0.0	12.5	24
Ethyl alcohol	25.0	91.8	12

TABLE 14

Copper Replacements Secured with the Various Salts

Copper salt	Actual replacements Percent	Actual and indicated replacements Percent	Experiments performed
Acetoacetic ester	16.7	49.0	204
Palmitate	19.5	45.8	144
Abietate	15.8	34.3	108
Anisate	27.8	62.5	72
Capronate	8.3	57.0	72
Cinnamate	33.3	40.0	60
Margarate	18.4	30.0	60
Phthalate	19.5	61.3	36
Camphorate	37.5	58.3	24
Isovalerianate	29.2	58.3	24
Laurate	12.5	25.0	24

TABLE 15

Copper Replacements Secured with the Various Metals

Metal	Actual replacements Percent	Actual and indicated replacements Percent	Experiments performed
Cd	77.8	77.8	9
Pb	55.0	73.3	69
Zn	49.3	71.0	69
Bi	29.0	53.6	69
Mg	23.2	50.8	69
Co	21.8	55.1	69
Sn	17.4	46.5	69
Fe	14.5	39.1	69
Al	14.5	34.8	69
Ag	5.8	29.0	69
Sb	2.9	31.9	69
Ni	1.5	30.5	69
Hg	0.0	42.0	69

Comparison of Replacement Series of Metals in Non-Aqueous Liquids with Other Series

An interesting comparison, from the electrochemical standpoint, is given in Table 16. All the metals used in the

preceding experiments are arranged in the first column according to the actual percentage of cases in which they replaced copper. In the second column they are rearranged according to their percentage of actual and indicated replacement. With three minor changes, this column remains the same as the first. The third column gives Neumann's electrochemical series, together with the difference of potential between the metals and aqueous solutions of their salts.[1] The last column gives a series of metals as determined by their single potentials in normal potassium cyanide solution.[2]

TABLE 16

Comparison of Various Series of the Metals

Actual replacements Percent		Actual and indicated replacements Percent		Neumann's electrochemical series		N/1 KCN series	
Cd	77.8	Cd	77.8	Mg	+1.231	Al	+1.066
Pb	55.0	Pb	73.3	Al	+1.015	Zn	+0.992
Zn	49.3	Zn	71.0	Mn	+0.824	Mg	+0.935
Bi	29.0	Co	55.1	Zn	+0.503	Cu	+0.800
Mg	23.2	Bi	53.6	Cd	+0.174	Cd	+0.691
Co	21.8	Mg	50.8	Fe	+0.087	Sn	+0.503
Sn	17.4	Sn	46.5	Co	—0.015	Ag	+0.351
Fe	14.5	Hg	42.0	Ni	—0.020	Ni	+0.270
Al	14.5	Fe	39.1	Pb	—0.095	Pb	+0.147
Ag	5.8	Al	34.8	Bi	—0.315	Fe	—0.006
Sb	2.9	Sb	31.9	Sb	—0.376	Bi	—0.020
Ni	1.5	Ni	30.5	Sn	—0.085	Pt	—0.220
(Hg)	0.0	Ag	29.0	Cu	—0.515	C	—0.456
—		—		Hg	—0.980		—
—		—		Ag	—0.974		—
—		—		Pd	—1.066		—
—		—		Pt	—1.140		—
—		—		Au	—1.356		—

It must be remembered that cadmium was used in only about 13 percent of the total number of experiments; still in

[1] Zeit. phys. Chem., 14, 229 (1894).

[2] These results are the average of the findings of a class in Applied Electrochemistry at this University in 1907.

these it gave as good results, or better, than did lead and zinc. Mercury falls at the bottom of the first column, because of its amalgamating properties. Its position in the second column is more probably its proper place. The only other differences are the shifting up of cobalt in the second column and the shifting down of silver. The reason for this is unknown.

It is very evident from a comparison of the last three columns that the replacing power of the metals is not a fixed property of the metals themselves, but is largely dependent on the chemical nature of the solution in which the replacement occurs. The three series do not show even approximately the same sequence of metals, in the majority of instances. While there seems to be some connection between the electrical potentials of the metals and their basicity or replacing power in aqueous solutions, this does not appear in non-conducting solutions. Replacements occur, but these evidently cannot be ascribed to "electrolytic dissociation," for the solutions are insulators.

Effect of Small Amounts of Atmospheric Moisture in Replacement Experiments

Thinking that possibly some of these reactions might be due to moisture absorbed by the solutions from the air, over one hundred duplicates were run in sealed tubes. In these cases, the same results were always obtained as in the open tubes and therefore no further precautions were taken in this direction, except in the cases where solvents were known to be hygroscopic. All the copper salts and most of the solvents showed no such tendency. This confirms results on the effect of small amounts of water as previously found by other investigators.[1]

Metal Replacement in Fused Salts

Sammis[2] found that fused copper oleate and palmitate will both copper-plate lead instantaneously. The tempera-

[1] J. L. Sammis: Jour. Phys. Chem., 10, 608 (1906); J. H. Mathews: Ibid., 9, 663 (1905).

[2] Sammis: Loc. cit., p. 612.

tures at which these salts melt preclude all possibility that replacement is due to the presence of moisture. In order to investigate such reactions farther, it was first determined whether the copper salts available could be fused without decomposition, by gradually heating them in an oil-bath.

Copper acetoacetic ester became brown at 170° C and an odor resembling that of some of the higher esters was detected. This was probably acetoacetic ester, which boils at 181° C. On higher heating, the salt decomposed entirely, leaving copper and some copper oxide. Copper cinnamate became green at 160° C and decomposed at 250° C. The phthalate showed a similar change at 200° and broke up at 280°. The abietate, capronate, anisate and isovalerianate decomposed respectively at 190°, 160°, 255° and 350°. Copper camphorate turned from light blue to green at 175°. This color change was completely reversible, depending on the temperature. The salt decomposed at 250°. Copper palmitate was entirely fused to a dark green, oily liquid at 200°. This was also the case with the stearate and margarate at 240° and 255° respectively. The last three salts were used in the following tests. Pieces of metal were scraped clean, held in the molten salt from one to three minutes, taken out, the adhering mass of solidified salt removed mechanically or by solution, and the metal surface examined for copper. The results are given in Table 17.

In all three salts, lead, zinc, tin and bismuth gave especially good results, a heavy coating of copper depositing immediately. The usually strongly basic magnesium and sodium were surprisingly inactive, behaving about like nickel and cobalt. The inaction of aluminum and iron is also perplexing, unless it is assumed that their surface was protected by a film of oxide. There is, however, no experimental evidence whatever upon which to base such an assumption. These results are important from the fact that the chemical reactions are as vigorous and instantaneous as similar replacements in aqueous solutions; and yet they take place in liquids that are completely anhydrous and non-conducting.

TABLE 17

Copper Replacement in Fused Salts

Metal	Copper palmitate, 220°	Copper stearate, 250°	Copper margarate, 260°
Pb	Coppered	Coppered	Coppered
Zn	Coppered	Coppered	Coppered
Sn	Coppered	Coppered	Coppered
Bi	Coppered	Coppered	Coppered
Cd	Coppered	Coppered	Coppered
Sb	Coppered	Coppered	Coppered
Hg	Coppered[1]	Coppered slightly[1]	Coppered[1]
Co	Coppered	Coppered slightly	Not coppered
Ni	Coppered slightly	Not coppered	Not coppered
Mg	Coppered slightly	Not coppered	Not coppered
Na	Not coppered	Coppered	
Al	Not coppered	Not coppered	Not coppered
Ag	Not coppered	Not coppered	Not coppered
Pt	Not coppered	Not coppered	Not coppered
Fe	Not coppered	Not coppered	Not coppered

The results do not agree very closely with what would be expected from the position of these metals in the ordinary electrochemical series. In order to see what agreement there might be with that series, if fused salts that *do* conduct were used, the following experiments were carried out.

Metal Replacement in Conducting Fused Salts

The action of metals upon solutions of silver nitrate has been carefully studied by Senderens.[2] Upon *fused* silver nitrate but little has been done. The salt is easily melted at about 218° C without decomposition.

Calcium reacted with the fused salt with evolution of

[1] Mercury caused the molten mass to become brownish-black and spots of copper were seen floating on the surface of the metal. The mercury was removed, washed thoroughly with amyl alcohol and carbon tetrachloride until it was perfectly clean and white. It was then volatilized from a white porcelain surface and left a grayish-black spot, very thin and shiny. This was dissolved in nitric acid and gave a copper test with potassium ferrocyanide. A blank test left a perfectly clean porcelain surface.

[2] Bull. Soc. chim. Paris, [3] 15, 208, 691 (1896); 17, 271 (1897); Comptes rendus, 104, 504 (1887).

light, and metallic silver was thrown out. Magnesium showed apparent decomposition around the metal and nitrogen peroxide was given off on continued heating. The magnesium entirely disintegrated and white metallic silver was formed. The fused mass was deliquescent when cold, indicating the presence of magnesium nitrate. This reaction took place below the melting point of magnesium.

Cadmium and lead both gave vigorous reactions and nitrogen peroxide was liberated, because the temperature was above that of the decomposition point of the nitrates of these metals. Both precipitated metallic silver. The reaction of zinc was sufficiently exothermic to keep the silver nitrate melted and oxides of nitrogen were liberated. The zinc strip was disintegrated and silver precipitated. Tin melted in the fused silver salt and a coating of black stannous oxide formed over the bright metal, but the change was rather slower than the similar reaction in aqueous solution. Cobalt was covered with a dark gray tarnish, which gave a test for silver.

Gold, aluminum, iron and silicon gave no results. Copper darkened a little in the nitrate, but this dark gray, metallic stain gave no test for silver; nor was any copper found in the silver nitrate afterward.

The effect of introducing metals into a fused mixture of silver nitrate and potassium nitrate was then tried. Copper, magnesium, iron, aluminum, zinc and cobalt gave the same results as in fused silver nitrate alone. The action of the zinc was much less vigorous than before. The salt around the cobalt took on a peculiar lavender color, but this disappeared with rise of temperature.

Very little was done with fused mercuric chloride, as it was already known that many of the metals will reduce it to mercurous chloride, and even to mercury, when heated. Copper was tried and was mirrored with mercury at once. Gold remained unchanged. Silver was coated heavily and much silver was found in the fused salt afterward. This

result was unexpected, as silver is generally more electronegative than mercury in aqueous solutions.

Fused silver chloride (460° C) was next tried. Copper, tin, iron, aluminum, nickel, cobalt, bismuth, magnesium, zinc, calcium and lead decomposed the salt and either free silver was thrown out or an alloy was formed. Gold, platinum and silicon produced no effect. The case of the aluminum was interesting because it gave no reaction until melted. Suspecting that this passivity might be due to an oxide film, the metal was scratched beneath the fused silver chloride with a glass rod. Vigorous reaction immediately resulted and dense white fumes of aluminum chloride were copiously evolved. In the case of the iron, the cold fusion mass was reddish-brown and in the case of cobalt bright green. The product resulting from the action of the zinc was strongly hygroscopic. As soon as the silver chloride fused, calcium reacted with it with strong evolution of light.

The results when silver chloride was fused with sodium chloride were practically the same as when the silver salt was used.

In fused zinc chloride (262° C), magnesium threw out metallic zinc. Copper, aluminum, and lead did nothing. The lead melted and could be alloyed with copper beneath the fused chloride, as one would naturally expect.

Fused copper chloride decomposes rapidly, yielding chlorine and cuprous chloride. According to Moissan, some cupric oxide is also formed. The fused mass was dark brown, due to anhydrous cupric chloride. Iron, aluminum (on scratching), magnesium (explosively), and calcium, all reacted with the fused mass with increasing violence. Gold, silver, silicon and nickel produced no action.

Fused sodium chloride gave no reaction with either silicon or magnesium.

Fused calcium chloride (710°–806°) gave no results with copper, graphite, silver, nickel, cobalt, iron, aluminum and antimony. The last two metals melted and oxidized. Potassium and sodium reacted violently. Magnesium melted,

and the fused calcium chloride seemed to boil all around the liquid metal. This was accomplished by a continual crackling sound and these tiny explosions were often attended with flashes of fire. Evidently some of the freed calcium was reaching the surface and burning. Silicon gave results similar to those of magnesium, but these were even more energetic. It is known that alkaline chlorides, at high temperatures, react with silicon to form silicon tetrachloride.[1] And when the tetrachloride is passed over hot silicon, a hexachloride (Si_2Cl_6) is formed; the vapor of this substance will burn when heated in air.[2] The presence of a little of this vapor may account for some of the phenomena observed. However, as exactly similar results were obtained with magnesium, where there could be no silicon chloride, the indications are that it is metallic calcium which is liberated and burns. After cooling, the fused mass would not all dissolve in boiling water, but hydrochloric acid would dissolve it with effervescence. This would show that some calcium oxide had probably been formed, and some of this was converted into carbonate during the boiling in water. Much of the liberated calcium doubtless alloyed with the silicon.[3] This probable alloy reacted with water very slowly (more rapidly if warm), indicating the presence of calcium.

The results of this series of experiments are almost completely in accord with what would be expected as to the relative basicity of the metals concerned, judging from their action in aqueous solutions. But whereas in water solutions all more electropositive metals displace all less positive, in non-aqueous fused salts this is not always the case.

Solution of the Precipitated Copper by the Solvents Used

The power of an acid to conduct the electric current and its ability to exchange its hydrogen for a metal have been

[1] Baudrimont: Jour. Pharm. Chem., [4] 40, 161 (1871).

[2] Troost and Hautefeuille: Ann. Chim. Phys., [5] 7, 463 (1876): Comptes rendus, 73, 443 (1871).

[3] Wöhler: Liebig's Ann., 125, 255 (1863); 127, 257 (1863): Moissan: Bull. Soc. chim. Paris, [3] 21, 865 (1899).

thought to be associated usually with the presence of aqueous solutions. Indeed the presence of water has been assumed as a necessary condition for both phenomena. The electrolytic dissociation theory has accounted for both by postulating the existence of ions, and has affirmed that an acid that could not furnish ions to carry a current, could not dissolve a metal. An insulating acid like oleic should show no dissolving power whatever, to accord with the theory. Therefore it might be assumed that when oleic acid was used as a solvent in the foregoing experiments, replaced copper would be entirely safe from re-solution, since the acid had not the slightest conductivity. However, it was discovered accidentally that many of the metals do dissolve in pure oleic acid to a considerable extent. While the action is slow in most cases, in some instances it is as vigorous as that of aqueous hydrochloric acid solutions on zinc.

In all cases where oleic acid was used as the solvent, replacements of copper were very frequent. It was also noticed that there were many cases where chemical action seemed to be taking place and yet no coating of metallic copper was visible. For instance, the solution would lose its green color wholly or in part, or a light colored precipitate would settle out, or the solution would solidify, or the metal would tarnish or disintegrate. This suggested the explanation that the solvent might be capable of dissolving metallic copper as fast as it was thrown out and direct evidence of replacement would be destroyed or weakened by this secondary reaction. This led to a series of experiments to ascertain the solubility of copper and other metals in some of the solvents used.

Solubility of Copper in Oleic, Palmitic and Stearic Acids

Clean pieces of copper were placed in two samples of oleic acid, obtained respectively from Kahlbaum and Bausch & Lomb. Another piece was put in benzaldehyde. All three solutions soon became deep green in color at room temperatures. In the case of the oleic acids, hydrogen was visibly evolved. It was thought that this solvent action of

the acid might be due to small amounts of inorganic acids, but none were found. Both samples of oleic acid were tested with anhydrous copper sulphate for water. Their conductance was less than 2×10^{-10}. Samples of each were shaken up with distilled water and the filtered water was tested for hydrochloric, sulphuric and nitric acids. As a farther check, oleic acid was well shaken with a weak potassium hydrate solution. White potassium oleate precipitated out. Any mineral acid, present in traces, would be neutralized by this treatment. Yet some of the unsaponified acid, which rose to the surface on standing, dissolved copper as well as ever. It is therefore decided that when no replacement is observed in oleic acid solutions, this is not conclusive, because of the solubility of the metal replaced.

Stearic and palmitic acids (Schuchardt) were melted on carefully cleaned copper foil and kept fused for half a minute. On cooling, they were both green. They were subjected to the same process for removing traces of mineral acids as was the oleic acid, and still both became green on copper foil. Cottonseed oil, which is essentially glyceryl oleate, would not dissolve copper in the least.

A piece of clean zinc was placed in some of Kahlbaum's oleic acid. On warming, after a short period of induction, hydrogen was more vigorously evolved than in the case of copper. The solution was allowed to stand over night so that any traces of strong acids might be removed. But on warming again, the action was just as vigorous as at first.

A quantitative examination of the solubility of copper in oleic acid was then undertaken and the first experiment extended over two years. Most of the time the solution was kept at room temperatures, though occasionally it was heated as high as 75° C. The results were as follows:

TABLE 18
Solution of Copper in Oleic Acid

Weight of copper Gram	Date	Percent loss	Time elapsed
0.4020	5/ 9/1907	—	—
0.3940	5/20/1907	1.99	11 days
0.3526	6/ 7/1907	12.29	28
0.3024	6/16/1908	24.77	402
0.2814	11/ 2/1908	30.00	538
0.2145	5/20/1909	46.64	737

The amount of oleic acid with which the experiment started was 3 cc, but this became slightly less each time, as the metal was removed for weighing. On the last date, the solution had become as viscous as glycerin. It was very dark green and perfectly opaque (in an ordinary test tube). The tube was kept tightly corked during the whole time. About two-thirds of the the available oleic acid was taken up by the metal and the green liquid was a saturated solution of copper oleate in the remaining third. The whole solution became a buttery solid on cooling below 50° C.

Preparation of Pure Oleic Acid

This curious behavior of oleic acid toward copper raised the question of how it would act toward other metals. In order to be surer of its purity, a quantity of oleic acid was prepared in the laboratory. High grade cottonseed oil was saponified with potassium hydrate and the oleic acid was then thrown out of solution with tartaric acid. It was nearly colorless and was a solid at room temperature. The other acids possibly present were palmitic, stearic and linoleic.[1] The melting points of these are: palmitic 62°, stearic 71°–71.5°, linoleic under 18°, and oleic 14°[2].

The purity of the cottonseed oil used was tested by cooling. It began thickening at —5° and was like glycerin and opaque at —10°. Palmitin solidifies at 58°–66°, stearin

[1] Leach: "Food Inspection and Analysis," p. 418.
[2] Lewkowitsch: "Oils, Fats and Waxes," p. 24.

at 55°–72°, and olein at —6°. The amount of palmitin and stearin in the oil must therefore have been very small.

The mixture of oleic acid with these small amounts of other acids was distilled from a double necked distilling flask under a pressure of 10 mm and at a temperature of 210°–220°. This boiling point agrees very closely with the results of Krafft and Nördlinger on pure oleic acid.[1] The distillate was cooled with running water. It solidified into a pure white mass. At room temperature, this was put on a suction filter and an oil removed which was very slightly yellowish in color. The very small amount of white solid left on the filter had a melting point of 60°, which agrees with that of palmitic acid.

The oleic acid thus prepared showed the following constants: Slightly acid toward litmus. Slightly yellow, when in large quantity. Conductivity less than 2×10^{-10}. Melting point 13.5° C. (Gottlieb gives 14°.) Specific gravity was 0.8953 at 14° C. (Chevreul gives 0.898 at 14°.)

Solubility of Metals in Oleic Acid

A number of metals were cleaned and introduced into this pure oleic acid. Sodium, potassium and calcium immediately evolved hydrogen at room temperature and at a rate sufficient to enable it to be exploded in the test tube. Other metals were heated to 100° in the acid and, arranged in the order in which they were most vigorously attacked, they are copper, zinc, lead and cadmium. Silver and magnesium acted very slowly; that is, a few small bubbles of hydrogen were seen on the surface of the metal only after five minutes of heating at 100°. Aluminum, nickel, cobalt, antimony, iron, bismuth, tin, mercury and platinum were apparently unaffected.

It was repeatedly found that a test tube containing copper and oleic acid gradually lost weight, which was too much to be accounted for by the slight evaporation of the acid itself. In a week, a tube containing only oleic acid and weighing 3.5234 grams lost no appreciable weight; whereas one containing oleic acid and copper and weighing 3.7040

[1] Ber. chem. Ges. Berlin, 22, 819 (1889).

grams lost 0.0027 gram during the same time. In this 3.7040 grams there were 0.9116 gram of acid, or 0.0032 gram of replaceable hydrogen. The loss in weight is explained by the partial liberation and escape of the replaceable hydrogen. The reaction is probably expressed by the equation,

$$Cu + 2C_{17}H_{33}COOH = (C_{17}H_{33}COO)_2Cu + H_2.$$

Two series of experiments were undertaken to study further the quantitative side of this solvent action of oleic acid toward metals. The first is summarized in the following table. In each case 1 cc of acid was used, but the weights and exposed surface areas of the metals differed, so the results are not to be rigidly used for purposes of comparison. In a general way, however, they show the relative affinities of the metals for the acid. The metals were in contact with the acid for 120 hours at room temperature and then 10 hours more at 90°–100°. The copper solution became perceptibly greenish in twenty minutes (23° C). During the same time, the surfaces of the zinc, lead, cadmium and bismuth became dulled; tin, iron, magnesium and silver remained bright; and a white solid separated out in the case of the mercury.

TABLE 19
Solution of Metals in Oleic Acid

Metal	Wt. before in grams	Wt. after in grams	Loss in gram	Condition of metal afterward	Condition of solution afterward
Pb	0.2402	0.2112	0.0290	Grayish-white coating	Yellow. White ppt.
Hg	11.7984	11.7792	0.0192	—	Grayish-white ppt.
Cd	0.2705	0.2539	0.0166	Grayish-white coating	Yellow. White ppt.
Zn	0.1920	0.1785	0.0135	Grayish-white coating	Solid. Light yellow.
Bi	1.4032	1.3921	0.0111	—	Yellow. White ppt.
Sn	0.2155	0.2075	0.0080	Tarnished	—
Cu	0.1305	0.1277	0.0028	Bright	Deep green
Mg	0.0317	0.0294	0.0023	White coating	Yellow
Fe	0.0741	0.0734	0.0007	Bright	Reddish-brown
Ag	0.0769	0.0768	—	Bright	Yellow-brown

Blank oleic acid—light yellow (slight oxidation).

The experiments were repeated with a much longer time of exposure, especially at the higher temperature, and a much larger number of metals was used, including some of the more uncommon ones. Again, care must be taken in making any comparisons other than the most general. Half a cubic centimeter of oleic acid was used in each case. The duration of the experiment was 290 hours, during 60 of which the temperature was between 90° and 100° C. Then the metals were taken from the solution, washed successively in amyl alcohol, ethyl alcohol and ether and weighed.

TABLE 20

Solution of Metals in Oleic Acid

Metal	Wt. before in grams	Wt. after in grams	Loss in gram	Solution	Metal
Pb	0.5227	0.4635	0.0592	*a, d*	
Na	0.0874	0.0425	0.0449	*a, d*	*m*
Tl	2.2942	2.2518	0.0424	*f*	
Ca	0.1066	0.0732	0.0334	*a, d*	*m*
Cd	0.4976	0.4683	0.0293	*a, d*	
Mn	0.9171	0.8895	0.0276	*a, d*	
Zn	0.1967	0.1727	0.0240	*a, d*	
Cu	0.0885	0.0728	0.0157	*g*	
Sn	0.1248	0.1114	0.0134	*c*	
Mg	0.0236	0.0132	0.0104	*b, c,*	*k*
Fe	0.0719	0.0622	0.0097	*b, h*	
Bi	0.9300	0.9209	0.0091	*b, d*	
Hg	1.4795	1.4720	0.0075	*c*	
In	0.0620	0.0581	0.0039	*d*	
As	0.2930	0.2898	0.0032	*c*	
W(powder)	0.2018	0.2003	0.0014(?)	*c*	
Te	0.2126	0.2112	0.0014	*d*	
Sb	1.0648	1.0641	0.0007	*d*	
Ni	0.0627	0.0624	0.0003(?)	*d*	
S	0.5178	0.4843	0.0335	*i*	*n*
Ir	0.0590	0.0590	—	*c*	
Au	0.1860	0.1859	—	*c*	
Pt	0.0563	0.0562	—	*c*	
Pd	0.0369	0.0368	—	*c*	
Ag	0.0759	0.0758	—	*c*	
Cr	0.1241	0.1240	—	*c*	
Mo	0.2722	0.2722	—	*d*	

TABLE 20—(*Continued*)

Metal	Wt. before in grams	Wt. after in grams	Loss in gram	Solution	Metal
Se	0.1299	0.1301	—	*c*	
Al	0.0697	0.0697	—	*c*	
Co	0.2909	0.2908	—	*d*	
K	0.1480	—	—	*a*, *d*	*m*
B	0.0105	—	—	*c*	*l*
Graphite	0.0709	0.0711	—	*c*	
Si	0.1001	0.1001	—	*c*	
P	0.2051	—	—	*j*	*o*

a—Solution became solid, when cold.
b—Solution thickened, when cold.
c—Solution color was same as the blank oleic acid.
d—Solution color became darker (light brown).
e—Solution color became quite brown.
j—Solution color became reddish-brown.
g—Solution color became deep green. Also opaque.
h—Solution became dark brown and opaque.
i—Solution became brown-black and opaque.
j—Solution became almost black and partly solidified.
k—Coated with a white film.
l—Small pieces of boron were used and some of them could not be recovered. Probably no loss in weight.
m—Virtually all dissolved. A few small pieces remained, but could not be weighed.
n—A rhombic crystal at first, but soon crumbled to powder. Some of the loss in weight was due to the slight solubility of sulphur in amyl alcohol and ether.
o—Still part of the yellow phosphorus left, but it could not be separated and weighed.

Solubility of Tin-Zinc Alloys in Oleic Acid

The solubility of a series of tin-zinc alloys, furnished by Mr. Alcan Hirsch, was similarly tested in oleic acid. The pieces used were practically all of the same surface area, so that the results are fairly comparable. The time of exposure and the temperatures were the same as before. Half a cubic centimeter of oleic acid was used in each case and the tubes were occasionally shaken. Hydrogen was evolved from the first. All the solutions became solid, on cooling to room temperature, toward the end of the experiment. With

the exception of the 30 percent tin alloy, the color became a little darker than that of the pure oleic acid, which was run as a blank. Examined with a lens, all the alloys appeared corroded, mainly in vertical streaks.

TABLE 21

Solution of Zinc-Tin Alloys in Oleic Acid

Metal Percent	Wt. before in gram	Wt. after in gram	Loss in gram
Zn (100)	0.1967	0.1727	0.0240
Zn (95)—Sn (5)	0.2354	0.1784	0.0570
Zn (90)—Sn (10)	0.1717	0.1257	0.0460
Zn (85)—Sn (15)	0.0959	0.0521	0.0438
Zn (80)—Sn (20)	0.2757	0.2299	0.0458
Zn (70)—Sn (30)	0.1852	0.1462	0.0390
Zn (60)—Sn (40)	0.2364	0.1957	0.0407
Zn (28)—Sn (72)	0.2188	0.1806	0.0382
Sn (100)	0.1248	0.1114	0.0134

Each alloy dissolved considerably more than either pure zinc or tin. The ability of each metal to resist solution—its chemical inertia, so to speak—is lessened by combining it with the other. Solubility increases with the percentage of zinc and this is to be expected, since pure zinc is more soluble in oleic acid than pure tin.

CONCLUSION

(1) From non-aqueous, non-conducting solutions it is possible to throw out metallic copper by means of lead, zinc, cadmium, tin, bismuth, antimony, mercury, silver, iron, nickel, cobalt, aluminum, magnesium, sodium, potassium and calcium. Platinum and gold alone gave no results. Other experiments performed show that there is every indication that other metals can be similarly replaced.

(2) Copper may be precipitated from fused organic salts by many of the common metals. Similar replacement may be effected in any fused salt, without the presence of moisture. Such reactions are often as vigorous and instantaneous as in aqueous solutions.

(3) A series of the metals arranged according to their relative basicity in non-aqueous solutions does not coincide with the electrochemical series. It is evident that such a series is dependent not alone on the relative affinities of the metals, but also upon the mutual relationship of the metals, the acid radicals and the solvents present in any given combination. The influence of the solvent is always a determining factor in the ability of any metal to throw another out of solution.

(4) The fact that so very many chemical replacements have been effected in liquids that are insulators is a certain indication that the apparent connection seen in aqueous solutions between such reactions and the electrical potentials of the metals is not a universal relationship. The chemical and electrochemical series alike are dependent on other factors than the metals themselves.

(5) Many metals are appreciably dissolved by oleic acid, an insulating medium, with concomitant evolution of hydrogen. Stearic and palmitic acids evidently act similarly.

This work was suggested by Professor Louis Kahlenberg and carried out under his direction. The author desires to take this opportunity to express his obligation to Professor Kahlenberg for the suggestion and guidance that have been given him throughout the prosecution of this research.

Laboratory of Physical Chemistry,
University of Wisconsin,
July, 1910

AN EXACT ELECTROLYTIC METHOD FOR DETERMINING METALS.

BY W. L. PERDUE AND G. A. HULETT

The electric current is our most effective means for obtaining metals from their compounds and the fact that metals may be separated from their solutions and each other at ordinary temperatures by this agent is the reason that so much attention has been given to electroanalysis. From a quantitative standpoint it is essential that the metal be deposited in a pure state and with a surface such that it may be readily freed from the electrolyte and brought into a condition to weigh without loss or oxidation.

The purity of the metallic deposit is affected by the presence of other metals in the solution. An electrolytic deposit undoubtedly contains all the metals which are in the electrolyte, but the relative amounts vary widely as they depend upon the decomposition potential of each ion upon the particular metallic surface presented to it and upon their concentration at this surface. The solubility and affinity relations of the metals for each other are also factors in determining the makeup of the deposit. It is possible however to make many excellent separations, especially where the decomposition potential of one metal is below that of hydrogen and the other above,[1] so that the hydrogen ion may act as a "safety valve." Or where it is possible to hold the voltage below the decomposition voltages of the metals which are not wanted in the deposit.[2]

Aside from the metallic impurities in electrolytic deposits there is the inclusion of the electrolyte in the deposited metal to be considered. There is very little information on this point and hardly any that is reliable. Considerable attention has been paid to the purity of the silver deposited in the silver coulometer. Analyses of these deposits for

[1] Bancroft: International Congress, 4, 703 (1904.)
[2] Sand: Jour. Chem. Soc., 91, 373 (1907.)

total silver have been made by Rayleigh and Sedgwick[1] and later by Richards, Collins, and Heimrod.[2] The results however were not concordant, so the authors finally resorted to the method of reheating the deposited silver in the dish in which it was determined and observing any change in weight. This method has been employed in all investigations on the silver coulometer, but the results have been contradictory and were not capable of interpretation as there was no information as to the nature of the impurity. A new method was devised by Hulett and Duschak[3] in 1908. The silver was detached from the platinum dish, brought into a vacuum where it could be heated to the melting point and the gases evolved were examined as to their nature and amount. A continuation of this work, which will soon be published, is giving good quantitative results and indicates that these inclusions are not of the same composition as the electrolyte and are large enough to be taken into account in accurate work. That all metals deposited in the solid state contain inclusions can hardly be questioned.

Even with a satisfactory method for determining the nature and amount of these inclusions it is still desirable to avoid them entirely. If the metal is deposited in the liquid state this is accomplished or if it is deposited in mercury and forms an amalgam there are no inclusions. The surface of a mercury or amalgam cathode is always a good one so that greater variations of current density and conditions in the electrolyte may be employed, also the metal is more easily and completely removed from the electrolyte with a mercury cathode. Mercury has been used as cathode for a long time in electro-analysis,[4] but not with the idea of avoiding inclusions. It has always been a difficult matter to get the amalgam into a weighable condition without a loss or

[1] Phil. Trans., 175, 411.

[2] Proc. Am. Acad., 35, 123.

[3] Trans. Am. Electrochem. Soc., 12, 255.

[4] W. Gibbs: Am. Chem. Jour., 13, 571; Luckow: Zeit. anal. Chem., 26, 113; Vortmann: Ber. chem. Ges. Berlin, 24, 2749.

oxidation of the metal deposited in it. The method described by Prof. E. F. Smith[1] is a great improvement on previous ones and is convenient for analytical pruposes, but washing the amalgam with water and other liquids which contain dissolved oxygen is bound to occasion some solution of mercury and the metal, also the necessary agitation of the amalgam causes some of it to divide into very fine globules which are easily washed away and escape detection.[2]

The fact that mercury does not wet its container, but allows a film of liquid to get beneath the mercury, is the chief source of difficulty encountered in removing the electrolyte and drying the amalgam, so our first attention was given to this point. Mercury does not ordinarily wet platinum but it is possible to amalgamate the inside of a crucible or cup so that mercury wets it completely and then the electrolyte never gets beneath the mercury. With this advantage only the upper surface of the amalgam need be considered in removing the electrolyte after the metal has been deposited. The electrolyte may of course be removed by displacement with water and the amalgam washed with water without any loss of mercury or metal by solution or oxidation *provided* we keep the amalgam cathode during this process. Furthermore, in the absence of a film of liquid between the amalgam and its container, this amalgam need not be disturbed or agitated so there is no tendency to form little globules which may be lost. The water is finally removed with a pipette and the drop or two of water which remains on the amalgam is allowed to evaporate in a vacuum desiccator over calcium chloride. One may readily observe the disappearance of the last trace of water and the dish and amalgam are ready to weigh in a few minutes. From the standpoint of accurate weighing, metallic surfaces are exceedingly well defined since there are no troublesome moisture films to contend against. Our desiccator contains

[1] Electro-Analysis, p. 58.

[2] H. J. Sand: Trans. Chem. Soc., 91, 373 (1907); also T. Slater Price: Trans. Faraday Soc., 3, 94–7 (1907).

a dish of mercury which maintains a vapor of mercury in the desiccator and so prevents a possible loss of mercury by evaporation. This vacuum method of drying mercury and amalgams will not do when they are in glass vessels or containers which they do not wet as the film of liquid beneath the mercury or amalgam evaporates irregularly and explosively, throwing mercury out of the container in a quite uncontrollable manner but when the mercury wets the container perfectly there is no trouble on this score.

We have made many blank experiments to test all these points. After a determination has been made and the weight of the crucible with the amalgam known, we have returned the exhausted electrolyte to the amalgam and turned on the current. After repeating all the manipulations the crucible and amalgam have been reweighed, this gives the errors of the method.

Weight of the cup and amalgam	Weight after the blank
101.4909	101.4908
109.6732	109.6733
132.3499	132.3498
98.0254	98.0254

These are typical trials and as we are determining two to three grams of cadmium in each case it is seen that the errors are less than 1 part in 20,000. The vacuum correction is easily applied, and we are therefore in a position to determine the mass of metal in a given solution in a satisfactory manner and to know that nothing but the metal has been weighed.

The solubility of platinum in mercury is very small, so that crucibles which have been amalgamated and used for this purpose may be readily cleaned with acids at any time. The loss of platinum is small and the crucibles are not injured. Our method of amalgamating the inside of a crucible is to plate it electrolytically from a mercury cyanide solution; when washed out and rinsed with mercury it should

show a *continuous* film of mercury to within a centimeter of the top. It is very difficult to amalgamate some crucibles satisfactorily by this method but Mr. J. S. Laird of this laboratory has found that this may be readily done in all cases by filling the crucible with mercury to the desired height and then heating it nearly to the boiling point of mercury. After plating with mercury the crucible is washed with water, filled with the necessary amount of mercury and dried in the vacuum desiccator.

Fig. 1 shows the arrangement we employ in carrying out a determination. The funnel (*f*) has a wide stem (7 mm),

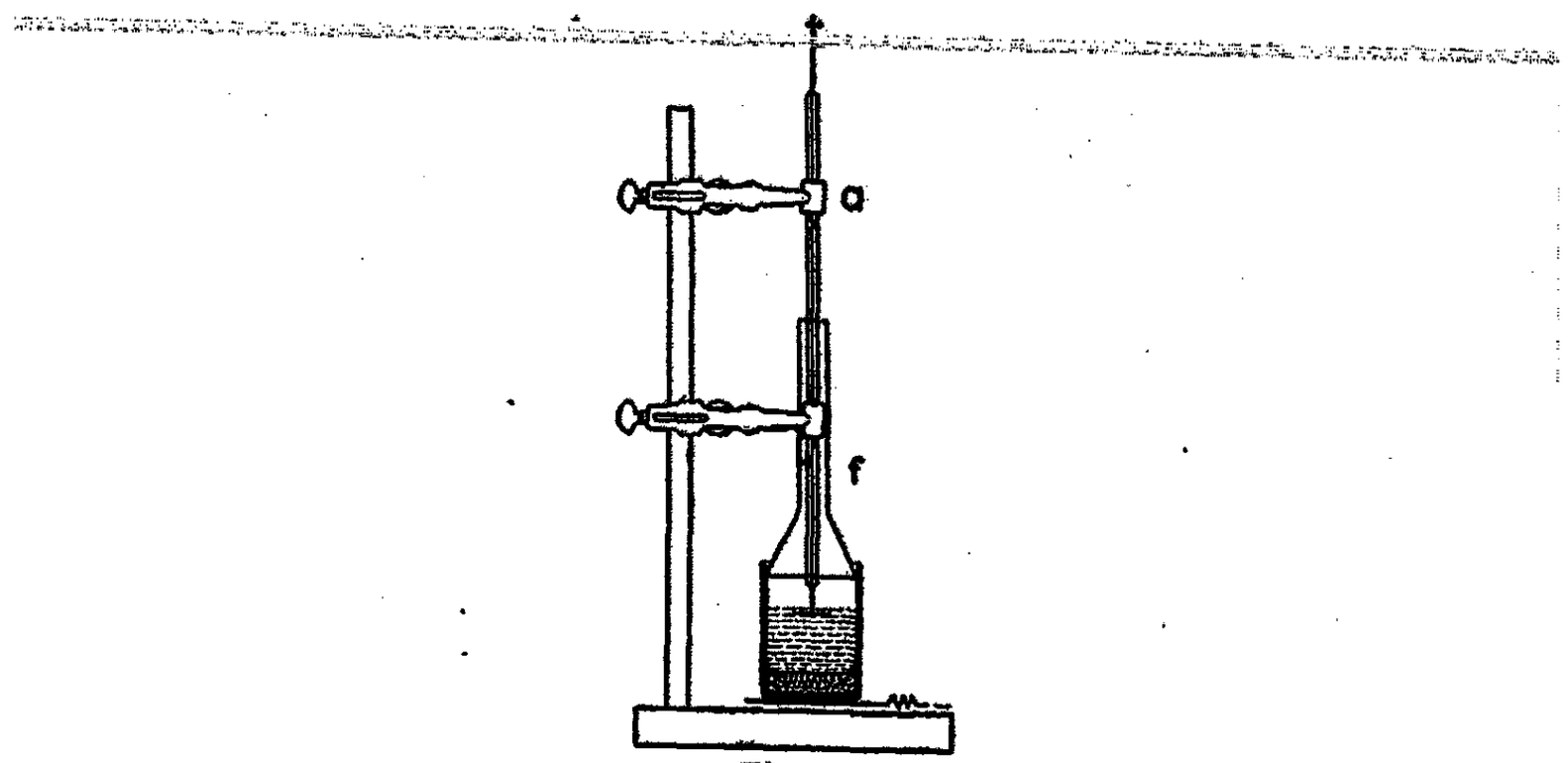

Fig. 1

while the rim fits nicely into the cup and thus prevents any loss of the electrolyte. The anode is a flat spiral made from platinum wire with the stem fused into a glass tube which is held by the clamp (*a*) and is independent of the funnel. The arrangement is such that the funnel may be raised clear of the cup without disturbing the anode. Towards the end of the electrolysis the current is increased to insure the complete removal of the metal. This is favored by the stirring of the electrolyte due to the increased generation of gas. The spraying thoroughly washes down the funnel and sides

of the cup so that it is seldom necessary to wash these through the top of the funnel.

After the metal has been completely deposited, the funnel is raised clear of the cup and the electrolyte removed with a large pipette while water is simultaneously run in. The stem of the pipette is drawn down to a thin tube and cut off at a convenient length while a rubber tube is attached to the upper end so that the pipette may be conveniently handled. A reservoir of distilled water is provided with an outlet tube, nozzle, and pinchcock so that water may be run into the cup at any desired rate and thus the electrolyte is displaced with distilled water without interrupting the current, and when the ammeter shows "zero" reading the displacement is complete and the amalgam throughly washed, but the amalgam is still cathode by 10 or 12 volts and under these conditions there can be no loss of mercury or metal by oxidation or solution. Since the amalgam is not disturbed or agitated there is no tendency to form fine globules. The water is now removed with the pipette, the anode raised, and after attention has been given to the outside of the crucible it is put into the vacuum desiccator and is ready for weighing in a short time.

Analysis of Cadmium Sulphate.—$CdSO_4.8/3H_2O$ is an exceptionally well defined and stable salt which may be obtained in a high state of purity as will be shown in the following article. We have determined the percent of cadmium in this salt with the apparatus and methods just described and offer a few of the preliminary determinations to give an idea of the possibilities of the method:

	Mass $CdSO_4.^8/_3H_2O$	Mass Cd	Percent Cd
1	8.2375	3.6076	43.795
2	9.2857	4.0668	43.798
3	6.5312	2.8609	43.804

A detailed study of the properties and composition of this compound will be given in the following article.

Cadmium is one of the most soluble of the metals in mercury (5.6 percent), but some metals have only a very small solubility and in such cases a solid amalgam soon forms and floats on the surface of the mercury cathode. The metal soon grows up and away from the mercury and may include some of the electrolyte. By agitating the mercury during the deposition of the metal this difficulty is overcome, for any motion of the mercury not only prevented the "treeing" of the metal but kept the amalgam covered with a film of mercury which prevents inclusions. We have accomplished this result by rotating the cathode crucible during the electrolysis.

The accompanying sketch is self-explanatory. The cup and shaft were turned from solid brass while the shaft works in a bronze socket which is fitted into a lead base. The platinum cathode cup or crucible fits exactly into the

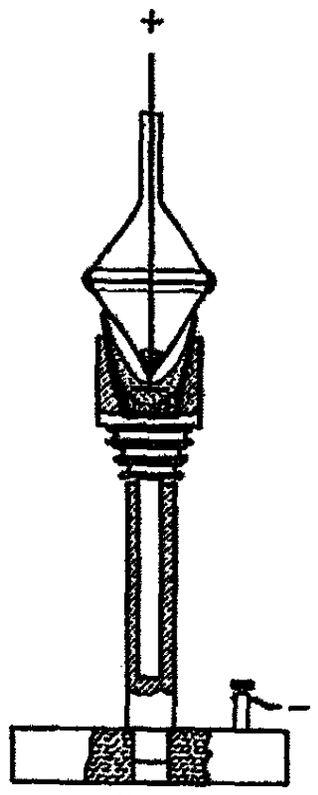

Fig. 2

brass cup and must rotate without vibration. The platinum spiral which serves as anode is fused into a little funnel and so arranged that the spiral is only a few millimeters from the mercury cathode when the crucible is at rest and at the

same time the sides of the funnel nearly touched the top rim of the crucible. The funnel is conveniently held by an inverted funnel (the two are held together by a rubber band) and electrical connections are made as indicated in the cut. Rotating the cup not only keeps any solid amalgam covered with mercury but causes the mercury surface to assume the form of a parabola which gives a large surface for a small amount of mercury. The electrolyte may be small in volume and the conditions are such as to allow a large current density and rapid deposition of the metal.

A few comparative determinations were made by determining the copper in equal portions of a copper sulphate solution and zinc in a zinc sulphate solution:

	Weight of zinc
1	0.4700
2	0.4699
3	0.4702

	Weight of copper
1	0.4793
2	0.4791
3	0.4794

A determination, weighings and all, took about 50 minutes and the average error seems to be about 1 in 4,000, and while zinc is fairly soluble in mercury (2.2 percent), copper has a solubility of only 1 part in 100,000.[1] Of course this method of rotating the cathode crucible offers many chances for accidental errors and cannot be compared in accuracy with the method previously described, but it has some advantages and is useful where great accuracy is not the main object.

Princeton University,
November, 1910

[1] Gouy: Jour. Phys., 4, 320.

CADMIUM SULPHATE AND THE ATOMIC WEIGHT OF CADMIUM

BY W. L. PERDUE AND G. A. HULETT

The most generally used analytical method of determining the equivalent weight of a metal is to determine the ratio of the metallic haloid to the silver haloid which is obtained from it. This method is not particularly direct but has been found to be the most satisfactory from an experimental standpoint and this is due, in a large measure, to the refinements in method introduced by Richards and his collaborators.

The estimation of a metal by electrolysis is one of the simplest and most direct methods for determining the ratio of a metal to its acid radical, haloid or to oxygen, but comparatively few such determinations have been made and not much weight has been given to those which have been made in this way. It would seem that the trouble has been due to the difficulties encountered in removing the metal completely from the solution in a sufficiently pure state and in obtaining it in a weighable condition without oxidation, loss or inclusions. In the preceding paper we have shown that it is possible to avoid these difficulties and the results obtained with cadmium sulphate were so concordant that it seemed worth while to make a more extensive study of this salt and the electrolytic method of determining its percent of cadmium.

Cadmium Sulphate

$CdSO_4.8/3H_2O$ is readily obtained in large clear crystals and it does not seem to be isomorphous with any other salts,[1] so that recrystallization offers an exceptional opportunity for bringing this substance to a high state of purity.

Ferrous and cupric sulphates seem to be isodimorphous with the crystallized $CdSO_4.8/3H_2O$,[2] but only very small

[1] Rammelsberg: Pogg. Ann., 115, 579; Kopp: Ber. chem. Ges. Berlin, 12, 911; Retgers: Zeit. phys. Chem., 16, 590.

[2] Retgers: Loc. cit.

amounts of these substances are taken up by the $CdSO_4$ crystals even when they are present in considerable concentration, but the method of purification we have used eliminated these metals.

Kahlbaum's cadmium sulphate was dissolved to about a 10 percent solution and H_2S was added until the precipitate was clear yellow. The solution was digested on the water bath with this precipitate until all the other heavy metals had been displaced and the precipitate was in a good condition to filter. The clear solution was now treated with H_2S until most of the cadmium was precipitated. The cadmium sulphide obtained in this way was thoroughly washed and treated with redistilled nitric acid until the sulphide was changed to sulphate and nitrate. A slight excess of sulphuric acid was now added and the liquid evaporated and heated until fumes of sulphuric acid appeared. The whole was now cooled and the cadmium sulphate drained to free it from the excess of sulphuric acid and then it was heated in a covered platinum dish in a specially constructed furnace until all the excess of sulphuric acid had been driven off. The cadmium sulphate obtained in this way was dissolved, filtered and repeatedly recrystallized. A saturated solution of cadmium sulphate has a density of 1.61 and is very viscous so that it was found best to start with a rather shallow solution 1 cm deep in the crystallizing dish and then the crystals formed on the bottom of the dish in a very satisfactory manner. The dishes were covered with filter paper and then placed in a constant temperature room so that the evaporation would be slow and uniform. These conditions gave us the maximum number of clear crystals but in every crop there were some cloudy ones which showed inclusions of mother liquor. The difference between the clear and cloudy crystals was very striking, the clear crystals were "water" clear in all parts and the microscope did not reveal a suggestion of inclusion. Only these clear crystals were taken for further recrystallizations and finally conductivity water and Jena glass or platinum dishes were used. The crystals were re-

moved from the dish with ivory forceps and wiped with sheet rubber (the rubber dam used by dentists). This was done because it was found that filter paper left the crystals slightly etched. This we think is due to the phenomenon of absorption. The filter paper coming into contact with the mother liquor on the face of the crystal, absorbs some of the dissolved cadmium sulphate and forms an undersaturated solution which attacks the crystals. With sheet rubber this action is a minimum and the faces of the crystals were left in a perfect condition. These crystals were perfectly stable in the dry air of our special balance room; a test extending over 14 days showed no change in weight.

Cadmium sulphate was described by Stromeyer[1] in 1822, who gave it the formula $CdSO_4.4H_2O$, and it has been the subject of extensive investigations since that time; but only recently[2] has the composition of these crystals been definitely settled. The trouble has been in determining the percent of water by glowing the crystals. Not until a loss of sulphate was detected, when the salt crystals were heated above a red heat, were the proper precautions taken and then more concordant results were obtained.

We find that $CdSO_4.8/3H_2O$ loses its water at a red heat and some SO_3 and then the CdO volatilizes. This difficulty was obviated by heating the crystals in an atmosphere which contained a little SO_3 and then we found that all the water could be driven off and the $CdSO_4$ remained perfectly stable up to at least 700°. Under these conditions the determination of the percentage of water in these crystals gave concordant results.

The determination of the percent of water of crystallization was carried out as follows: 5 to 7 grams of the crystals were placed in a tall narrow platinum crucible (15 mm by 65 mm). This crucible was furnished with a tight-fitting cover but a

[1] *Schweiggers' Jour.*, 22, 368.

[2] Follenius: Wied. Ann., 65, 348; Worobieff: Zeit. phys. Chem., 23, 557; Mylius and Funk: Ber. chem. Ges. Berlin, 30, 825; Kohnstamm and Cohen: Wied. Ann., 65, 348.

special perforated cover was used when the crucible was heated and through this perforation extended the small porcelain tube which delivered the air with a little SO_3. The crucible was heated in an electric furnace and was inside a quartz test tube which was also covered. The temperature was under excellent control and was measured with a thermocouple. The arrangement is sufficiently indicated in Fig. 1. The air which was passed over the crystals, while they

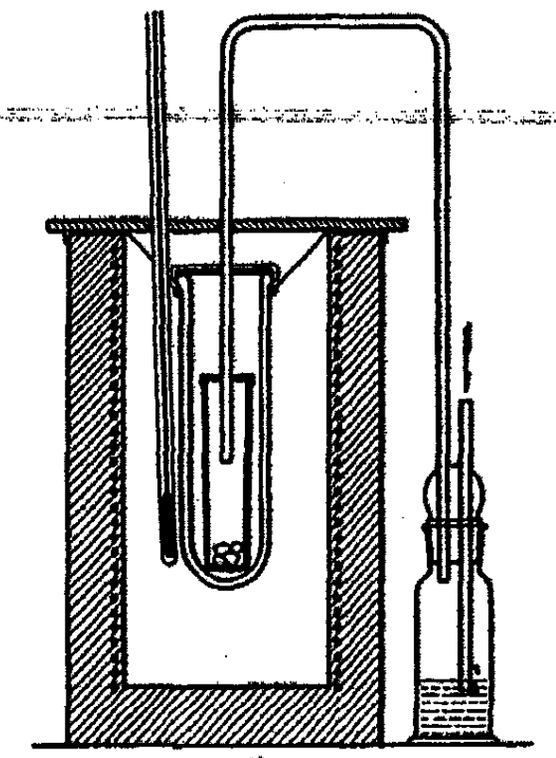

Fig. 1

were being heated, was filtered and dried and then passed through fuming sulphuric acid which gave the necessary SO_3 concentration so that there was no loss of SO_3 or CdO from the crystals. A series of experiments gave the temperature and time needed to remove the water of crystallization so that there was no change in weight when heated to a higher temperature. The range used was from 600° to 700°. After these conditions were worked out we undertook a determination of the water of crystallization in the purest crystals with the following results:

TABLE I

Percentage of H_2O in $CdSO_4.8/3H_2O$

No.	Mass $CdSO_4.8/3H_2O$	Mass $CdSO_4$	Mass H_2O	Percent H_2O
1	6.32863	5.14303	1.1856	18.734
2	6.72493	5.46507	1.25986	18.734
3	6.87537	5.58677	1.2886	18.742
4	5.65027	4.59205	1.05822	18.729
5	6.81125	5.53568	1.27557	18.727
6	7.34977	5.97274	1.37703	18.736
7	7.74837	6.29717	1.3572	18.727
8	7.8843	6.40718	1.47713	18.734
9	6.6100	5.37196	1.2480	18.730
				18.733

In the above table the percent of water amounts to 18.733, which is the arithmetical mean of nine determinations, the probable error of the mean is ±0.001, while the probable error of a single experiment is ±0.0045. The results seem to be entirely satisfactory, since we found that after the water had been expelled at say 670°, no further loss of weight was observed on heating to 700°.

The vacuum corrections used in the above table were calculated from the density of $CdSO_4.8/3H_2O$ and the density of the anhydrous $CdSO_4$. The determination of the density of $CdSO_4.8/3H_2O$ was carried out as follows: The crystals were weighed in a small platinum crucible suspended by platinum wires (0.1 mm) first in air and then in toluene. The toluene was dried and distilled and its density determined at 25° and 23.7° with a Sprengle-Ostwald pycnometer. Two determinations gave 3.0900 and 3.0902 as the density (M/V at 24°).

The density of the dehydrated crystals was obtained by heating the crystalline salt to constant weight, obtaining the weight of the dehydrated salt, and then placing it in a vacuum desiccator over calcium chloride where it remained in a vacuum of less than 1.0 mm for several hours. The vacuum desiccator was provided with a separatory funnel

so arranged that it was possible to allow the toluene to drop slowly onto the salt while it was still *in vacuo;* thus assuring a complete penetration by the toluene into all the interstices of the salt and eliminating any error due to included air. The crucible and contents were now removed and weighed in toluene. The density of the dehydrated salt was found to be 4.691 at 24°. The salt maintained the general contour of the crystals and did not fall into an amorphous powder but was quite hard. This greatly facilitates the ease of handling.

All weighings were made in a special balance room where the temperature was very constant, and where the moisture content of the air was under control. The weight of one cc of air in this room was 1.18 mg and the variations from day to day were negligible. The weighings were made by the Borda method of substitution: the set of weights used being very carefully calibrated, using a 100-gram *certified* standard whose density was 8.391; standard certified 1 and 10 gram weights were used as checks on the calibration at the proper places.

The specific volumes of both salts and weights are as follows:

$CdSO_4.8/3H_2O$	$D_{24} = 3.0901$	sp. vol. = 0.3236
$CdSO_4$ (anhyd)	$D_{24} = 4.691$	sp. vol. = 0.2132
Weights	$D = 8.39$	sp. vol. = 0.1190

Thus each gram of the crystals displaced 0.2064 cc more than the weights. The correction was $0.2046 \times 1.18 = +0.242$ mg per gram. For the anhydrous salt the corresponding correction was +0.123.

Determinations were next made of the metallic content of both crystalline and anhydrous cadmium sulphate. The percentage of cadmium in both of these substances was determined by the method and apparatus described in the previous article. A slight modification was made in that the crucible and mercury were put into a glass cup which was provided with a split cover as indicated in Fig. 2. The object of this cup was to make sure that there was no loss of electrolyte. After each determination the cup was rinsed

out and the washings tested for cadmium but none was ever found. We took particular pains to convince ourselves that all the cadmium was deposited in the mercury.

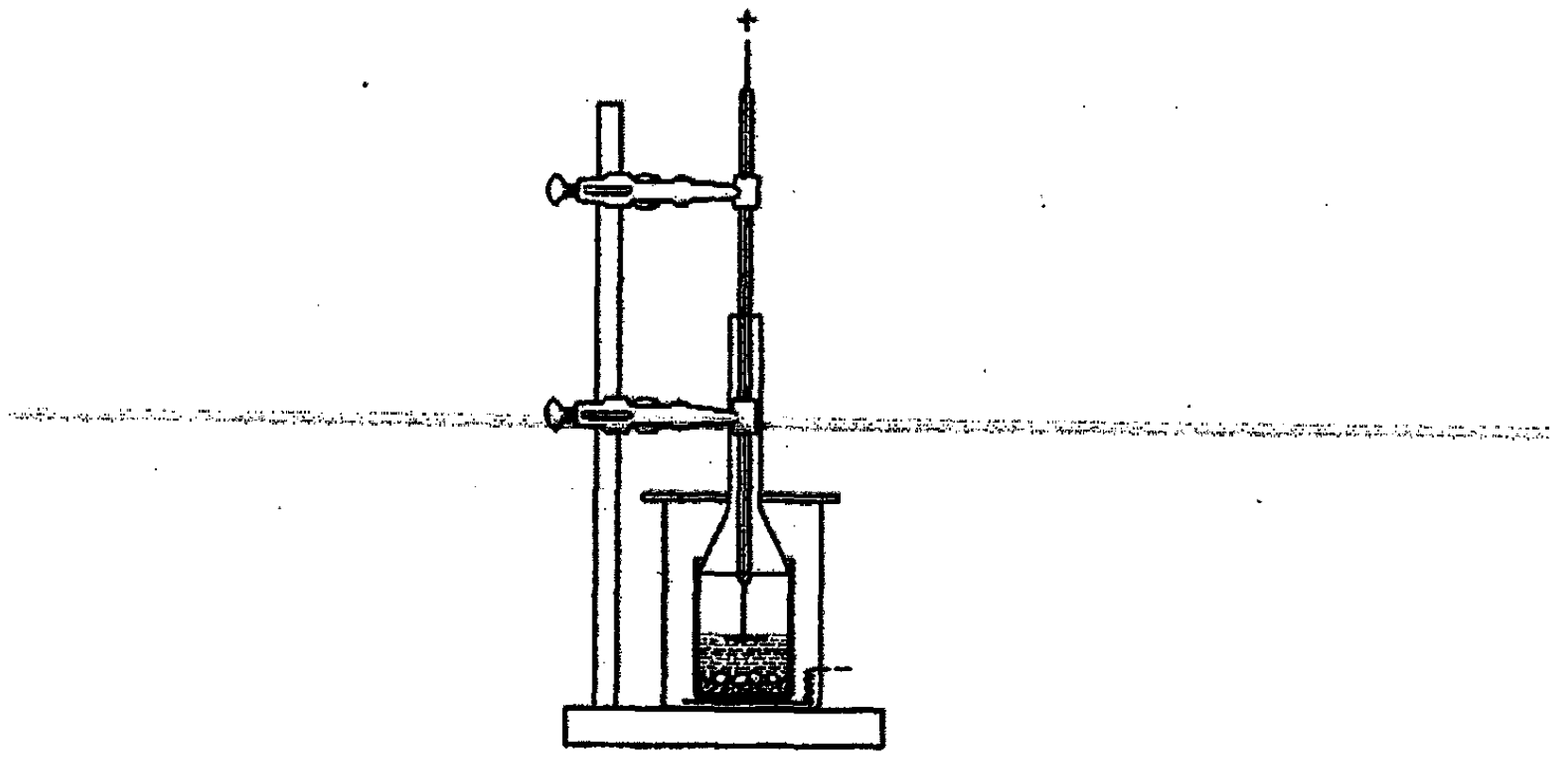

Fig. 2

The weighed crystals of $CdSO_4.8/3H_2O$ were placed directly on the mercury in the platinum crucible, then conductivity water was carefully added so as to cause as little solution of the sulphate as possible. A drop or two of sulphuric acid was added to aid in the conduction of the current and then the current was regulated so that there was no generation of gas at the cathode. The cadmium was thus deposited as fast as solution took place and the crystals melted away without cadmium appearing in the upper part of the electrolyte. When the cadmium was practically all deposited the current density was increased and the generation of the gas at both anode and cathode thoroughly stirred the electrolyte, rinsed down the sides of the crucible and at the same time the last trace of the cadmium was rapidly deposited. The electrolyte was removed as described in the preceding article (p. 152) and it was of course examined for cadmium by the ferrocyanide method, but no trace of the metal

was discovered in the exhausted electrolyte or any of the washings.

TABLE II

Percent of cadmium in $CdSO_4.8/3H_2O$

No.	Mass $CdSO_4.8/3H_2O$	Mass Cd	Percent Cd
1	7.90902	3.46335	43.790
2	9.07468	3.97434	43.796
3	7.32787	3.20936	43.796
4	6.48847	2.84186	43.799
5	5.11684	2.24157	43.808
6	8.02954	3.51755	43.807
7	5.08743	2.22827	43.799
			43.799

The determination of the amount of cadmium in the anhydrous sulphate was carried out in the manner alluded to under $CdSO_4.8/3H_2O$. The precaution was taken of thoroughly washing out the crucible in which the salt had been glowed and adding the washings to the electrolyte. The remainder of the process was carried out exactly as that of the crystallized sulphate.

TABLE III

Percent of Cadmium in $CdSO_4$

No.	Mass $CdSO_4$	Mass Cd	Percent Cd
1	5.14303	2.77196	53.897
2	5.46507	2.94566	53.898
3	5.58677	3.01076	53.891
5	5.53568	2.98276	53.883
7	6.29717	3.39295	53.880
8	6.40718	3.45255	53.887
9	5.37196	2.89457	53.883
			53.888

The vacuum correction for cadmium dissolved in mercury was readily obtained from the density of cadmium amal-

gams. Hulett and DeLury[1] found that the density of these amalgams was a linear function of the percent of cadmium, and at 24° could be expressed as follows: $D_{24} = 13.5364 - 0.0609 \times p$. From this it was easily found that a gram of cadmium dissolved in mercury displaced 0.107 cc of air and as a gram of brass weights displace 0.119 cc, the vacuum correction for each gram of cadmium dissolved in mercury was —0.014.

In the crystals we found 43.799 percent of cadmium as the arithmetical mean of seven determinations, and the probable error of this mean was ±0.0016. The percent of water by difference was 18.733 (see above). The 1911 atomic weights give cadmium 112.40, sulphur 32.07, hydrogen 1.008. This gives the molecular weight of $CdSO_4.8/3H_2O$ as 256.51 and its percentage composition as follows:

Cd	= 43.819
SO_4	= ....
$8/3H_2O$	= 18.729

These percentages are decidedly different from those found above. If, however, we take the atomic weight of cadmium as 112.30 the calculated percent is:

Cd	= 43.797
SO_4	= ....
$8/3H_2O$	= 18.736

which is in excellent agreement with our results.

If now we take 112.30 as the atomic weight of cadmium then the anhydrous $CdSO_4$ would contain 53.895 of cadmium, while we found in the above table 53.888 ± 0.0013. This difference is much greater than our experimental error. If the water had not all been expelled by heating the crystals the anhydride still contained water and the percent of cadmium would therefore have been low. Now the loss in weight of the crystals calculated as water was 18.733, the theoretical calculation being 18.736, which indicated a slight retention

[1] Jour. Am. Chem. Soc., 30, 1805.

of water by the anhydride but not sufficient to measurably affect its percent of cadmium. If the crystals had lost a slight amount of SO_3.CdO in spite of the presence of SO_3 in the air, then the observed loss would not all be water, but some of it would be SO_3.CdO and a correspondingly greater amount of water would then be left in the anhydride. The data which we had obtained gave us the possibility of testing this point by a simple calculation: In the experiments in Table III the crystals were weighed, glowed, and the percent of cadmium in the residual anhydride was determined. From this data we can also calculate the percent of cadmium in the original crystals and it gives 43.793 ± 0.001 instead of the 43.799 percent found in the unglowed crystals (Table II). This shows a loss of 0.006 percent of cadmium or 0.011 percent of $CdSO_4$ lost by glowing the crystals so that the total loss, 18.733 percent, was therefore composed of 18.722 percent of water and 0.011 percent of $CdSO_4$, consequently 100 grams of the crystals lost 18.722 grams of water and 0.011 grams of $CdSO_4$, while the remaining 81.267 grams of anhydride retained 0.014 gram of water (18.736 - 18.722) or 0.0172 percent of water. Now $CdSO_4$ which contains 0.0172 percent of water would show 53.888 percent of cadmium if the atomic weight of cadmium is taken as 112.30 We actually obtained in our results (Table III) 53.888 percent of cadmium in the anhydride.

In our endeavor to get pure anhydrous $CdSO_4$ we attempted to heat this substance to its melting point but as the SO_3, used to prevent decomposition, is measurably dissociated, long before the melting point of the salt is reached, it is therefore no longer effective in preventing measurable decomposition of the $CdSO_4$. From the constancy of the results and agreement with the calculated value (Table II) it seemed quite certain that all of the water had been expelled by heating to 700° but it is evidently a case of small compensating errors and shows how constant such errors may be.

The $CdSO_4.8/3H_2O$ crystals used gave evidence of being

very pure and free from all inclusions. The analysis of this substance points to 112.30 as the atomic weight of cadmium, a value so much lower than the accepted 112.40 that it seems desirable to check this result by determining the percent of cadmium in simpler substances such as the oxide and chloride.

Princeton University,
November, 1910

STUDIES IN THE ELECTROCHEMISTRY OF THE PROTEINS. IV. THE DISSOCIATION IN SOLUTIONS OF THE GLOBULINATES OF THE ALKALINE EARTHS

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I. Introduction

Not only the "basic" caseinates of the alkalies, but also the "basic" caseinates of the alkaline earths obey, in solution, the Ostwald dilution-law for the dissociation of a binary electrolyte.[1] From this and from other evidence pointing in the same direction, I have concluded that the molecule of a caseinate dissociates into two *protein* ions, in one of which the metal ion is bound up in a non-dissociable form.

The results of W. B. Hardy[2] have shown that the serum globulinate of sodium obeys, in solution, Ostwald's dilution law. The following data are obtained from Hardy's determinations of μ (the "apparent" molecular conductivity of the globulinate, cf. Pt. I of these studies) by multiplying each value of μ by the corresponding concentration.

TABLE I

Temperature 18°

m = Equivalent molecular concentration of NaOH neutralized to phenolphthalein by serum globulin $\times 10^5$	x = Conductivity of the solution in reciprocal ohms per cc $\times 10^6$
3125	1044
1563	627
782	353
391	189
98	54

[1] T. Brailsford Robertson: Part II of these studies, Journal of Physical Chemistry.

[2] W. B. Hardy: Jour. Physiol., 33, 251 (1905).

The proportion of alkali to globulin in each solution was 18×10^{-6} equivalents per gram. Such solutions are neutral to phenolphthalein, accordingly m, the equivalent molecular concentrations of alkali neutralized by the globulin is, in these solutions, equal to the total concentration of sodium.

In previous communications[1] I have shown that the Ostwald dilution-law for a binary electrolyte may be written

$$m = \frac{1.037 \times 10^{-2}}{v_1 + v_2} x + \frac{1.075 \times 10^{-4}}{G(v_1 + v_2)^2} x^2 \ldots\ldots\ldots (1)$$

where m is the equivalent-molecular concentration of the electrolyte, x its conductivity in reciprocal ohms per cc, G its dissociation-constant and v_1 and v_2 are the ionic velocities in cm per sec. per potential gradient of 1 volt per cm.

In applying equation 1 to solutions of salts of proteins we have no guarantee that m, the equivalent-molecular concentration of salt, is the same as m, the equivalent-molecular concentration of the alkali neutralized in its formation. But if not one, but ρ equivalent gram-molecules of globulinate are produced by the neutralization of one equivalent gram-molecule of NaOH then we may write equation 1 in the form

$$m = \frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)} x + \frac{1.075 \times 10^{-4}}{\rho G(v_1 + v_2)^2} x^2 \ldots\ldots\ldots (2)$$

in which m is now identical with the equivalent-molecular concentration of the alkali neutralized in the formation of the globulinate.[2]

Applying equation (2) to Hardy's results, enumerated in Table I and computing the constants $\frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)}$ and $\frac{1.075 \times 10^{-4}}{\rho G(v_1 + v_2)^2}$ from all of the observations by the method of least squares we obtain

$$m = 17.65\, x + 0.0115 \times 10^6\, x^2.$$

Inserting, in this equation, the observed values of x, we

[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907); 12, 473 (1908).

[2] Cf. number II of these studies, Ibid., 14, 601 (1910).

can compute the "theoretical" values of m, that is, the equivalent concentration of NaOH neutralized by the globulin which should, provided the sodium globulinate dissociates into *two* ions, correspond to the observed conductivities. In the following table the observed and calculated values of m are compared:

TABLE II

$m \times 10^5$ observed	$m \times 10^5$ calculated
3125	3095
1563	1559
782	767
391	375
98	99

It is evident that the correspondence between the experimental results and those which are indicated by the Ostwald dilution-law for a binary electrolyte is very close. It appeared to be of importance to ascertain whether the alkaline-earth salts of globulin, like those of casein, also obey the dilution-law for a binary electrolyte. Accordingly the following experiments were undertaken

II. Experimental

(*i*) *The preparation of the globulin.*

The globulin employed by Hardy in the experiments cited above was the "insoluble" globulin of ox-serum[1] prepared by precipitation from dilute serum through the cautious addition of acetic acid. I have employed the same globulin, precipitated, however, by passing a stream of CO_2 through the diluted serum, as recommended by Quinan. The following was the complete procedure.

Three liters of ox-serum were diluted with ten times their volume of distilled water and CO_2 was bubbled through the mixture for about half an hour. The globulin which was thus precipitated was allowed to settle in tall glass cylinders, the supernatant fluid being syphoned off after settling. The

[1] Cf. Quinan: Univ. of California Publ. Pathol., 1, 1 (1903).

precipitate was then washed with about 60 liters of distilled water, in two washings.

The globulin was then dissolved in a minimal quantity of N/10 KOH. This precipitate, after settling and the decantation of the supernatant fluid, was washed in 60 liters of distilled water in 6 successive washings, the precipitate, after each agitation with distilled water, being allowed to settle for 24 hours in the presence of toluol, after which the supernatant fluid was drawn off and the globulin suspended in a fresh quantum of distilled water. The thick suspension of globulin which was thus obtained after the final washing was kept, in the presence of toluol, in a stoppered bottle and used in this form, since globulin, if washed with alcohol and ether and dried, is redissolved only with difficulty. The suspension was, of course, always well shaken before withdrawing a sample.

Twenty-five cc samples of this suspension were placed in small and accurately weighed beakers: the fluid was then evaporated to dryness on a water bath and the residue was dried at 70° over H_2SO_4 until its weight became constant. Three determinations yielded the following results:

Determinations	Grams globulin in 100 cc of suspension
1	1.49
2	1.47
3	1.48
	Average, 1.48

In all, about 14 grams of globulin were obtained.

(*ii*) *Experimental results.*

The experimental procedure was the same as that described in previous communications.[1] Since Hardy's experiments were conducted upon sodium globulinate and at 18° and all my determinations were made at 30°, for purposes

[1] Part I of these studies, Jour. Phys. Chem., 14, 528 (1910).

of comparison, I have not only measured the conductivities of solutions of the globulinates of calcium, barium and strontium, but also those of solutions of the globulinate of potassium.

According to Hardy bases dissolve globulin in molecular, not equivalent-molecular proportions, about 10×10^{-5} equivalents of an alkali and 20×10^{-5} equivalents of an alkaline earth being required to dissolve 1 gram of globulin. The latter solutions are neutral to phenolphthalein, the former to litmus; but if 1 gram of globulin be dissolved in 20×10^{-5} equivalents of an *alkali* then the resultant solution is also neutral to phenolphthalein. That is to say, globulin combines with bases in *equivalent* molecular proportions to form solutions neutral to phenolphthalein, but in *molecular* proportions when the base is combined with the maximum quantity of globulin which it can hold in solution.

The solutions employed in the following experiments (except the solutions of strontium globulinate) were all prepared in the following manner. To 100 cc of the globulin-suspension (containing 1.48 grams of globulin) were added 29.6 cc of a hundredth-normal solution of the base and the resultant solution was diluted to 200 cc. One hundred cc of this solution was then diluted to 200, one hundred of the new solution to 200 and so on. The solutions of strontium globulinate were made up by adding to 25 cc of the suspension 7.4 cc of hundredth-normal $Sr(OH)_2$, diluting to 200 cc and then proceeding as described above.

All of these solutions were practically neutral to phenolphthalein, one-tenth of a cc of N/10 KOH sufficing to render 100 cc of the most concentrated solutions alkaline to this indicator.

The resistance-capacity of the conductivity-vessel employed was 0.1949. The conductivity of the distilled water (4.0×10^{-6}) has been subtracted from each of the observed conductivities. The following were the results obtained (temperature 30°):

TABLE III
Potassium globulinate

m = equivalent-molecular concentration of KOH neutralized by globulin × 10^5	x = conductivity in reciprocal ohms per cc × 10^6
296	116
148	64
74	33
37	18
18	9

TABLE IV
Calcium globulinate

m = equivalent-molecular concentration of $Ca(OH)_2$ neutralized by globulin × 10^5	x = conductivity in reciprocal ohms per cc × 10^6
296	45
148	26
74	15
37	9
18	4

TABLE V
Barium globulinate

m = equivalent-molecular concentration of $Ba(OH)_2$ neutralized by globulin × 10^5	x = conductivity in reciprocal ohms per cc × 10^6
296	49
148	27
74	16
37	9
18	4

TABLE VI
Strontium globulinate

m = equivalent-molecular concentration of $Sr(OH)_2$ neutralized by globulin × 10^5	x = conductivity in reciprocal ohms per cc × 10^6
74	17
37	9
18	5

III. Theoretical

Applying equation 2 to the results enumerated in Table III and computing the constants $\frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)}$ and $\frac{1.075 \times 10^{-4}}{\rho G(v_1 + v_2)^2}$ from all the observations by the method of least squares we obtain:

$$m = 19.62\, x + 0.0519 \times 10^6\, x^2$$

inserting in this equation the observed values of x and comparing the corresponding "theoretical" values of m we obtain:

TABLE VII

Potassium globulinate

$m \times 10^5$ observed	$m \times 10^5$ calculated
296	297
148	147
74	70
37	37
18	18

Applying equation 2 in the same way to the results enumerated in Table IV[1] we obtain:

$$m = 43.25\, x + 0.502 + 10^6\, x^2.$$

The observed values of m and those calculated from this formula are compared in the following table:

TABLE VIII

Calcium globulinate

$m \times 10^5$ observed	$m \times 10^5$ calculated
296	296
148	146
74	76
37	43
18	18

[1] Only the 1st, 2nd, 3rd and 5th determinations in Table IV were employed in the computation of the constants, the 4th being obviously somewhat in error.

Applying equation 2 to all of the results enumerated in Table V we obtain:

$$m = 42.61\,x + 0.369 \times 10^6\,x^3$$

The observed values of m and those calculated from this formula are compared in the following table.

TABLE IX

Barium globulinate

$m \times 10^5$ observed	$m \times 10^5$ calculated
296	297
148	142
74	78
37	41
18	18

Applying equation 2 to the results enumerated in Table VI we obtain:

$$m = 32.85\,x + 0.628 + 10^6\,x^3$$

whence

TABLE X

Strontium globulinate

$m \times 10^5$ observed	$m \times 10^5$ calculated
74	74
37	36
18	19

It is evident that the Ostwald dilution-law for a binary electrolyte holds good for the globulinates of the alkaline earths as well as for the globulinates of the alkalies; that the dependence of the conductivity of solutions of the globulinates of the alkaline earths upon their concentration, like that of the conductivity of solutions of the *caseinates* of the alkaline earths, is such as would be anticipated if they dissociated into *two* ions.

If we compute, from the values of the constants in equa-

tion 2, the values of $\rho(v_1 + v_2)$ for these globulinates we obtain.

For potassium globulinate	$\rho(v_1 + v_2)$	$= 52.9 \times 10^5$
For calcium globulinate	$\rho(v_1 + v_2)$	24.4×10^5
For barium globulinate	$\rho(v_1 + v_2)$	24.3×10^5
For strontium globulinate	$\rho(v_1 + v_2)$	28.5×10^5

The relation between the values of $\rho(v_1 + v_2)$ for the globulinates of the alkalies and of the alkaline earths is very similar to that which subsists between the corresponding values for the caseinates[1] and at once suggests the ratio 1 : 2.

The above values of $\rho(v_1 + v_2)$ for the globulinates of the alkaline earths are 50 percent less than the velocities of the metal ions themselves. As in the similar case of the caseinates, the only feasible explanation of this is that the globulinates dissociate into two complex *protein* ions and ρ is twice as great for the globulinates of the alkalies as for the globulinates of the alkaline earths.[2]

Since, at neutrality to phenolphthalein globulin neutralizes bases in equivalent molecular proportions, the molecule of calcium globulinate must, at this hydroxyl concentration, be twice as heavy as that of potassium globulinate. Hence representing the mode of dissociation of potassium globulinate (neutral to phenolphthalein) by the various schematic formulae:

$$\overset{1.}{KX^{++} + X(OH)_n'} \quad \overset{2.}{K_2X^{++++} + X(OH)_n''} \quad \overset{3.}{K_3X^{++++++} + X(OH)_n'''}$$

according to the number of —COOH groups concerned in the neutralization of bases, then the calcium globulinate (like calcium caseinate) must be represented by the corresponding schematic formulae:

[1] Cf. Part II of these studies. Journal of Physical Chemistry.

[2] The full discussion of this interpretation will be found in Part II of these studies, referred to above. I refrain from unnecessary reiteration of the argument.

1.

$$Ca\begin{cases} X^{+} \\ X^{+} \end{cases} + \begin{matrix} X(OH)'_n \\ X(OH)'_n \end{matrix};$$

2.

$$Ca_2\begin{cases} X^{++} \\ X^{++} \end{cases} + \begin{matrix} X(OH)''_n \\ X(OH)''_n \end{matrix};$$

3.

$$Ca_3\begin{cases} X^{+++} \\ X^{+++} \end{cases} + \begin{matrix} X(OH)'''_n \\ X(OH)'''_n \end{matrix}.$$

Assuming that schematic formulae (2) represent the true state of affairs, as they do in the case of the caseinates, we can at once understand why bases *dissolve* globulin in molecular and not equivalent molecular proportions. Evidently the molecule $KHX^{++++} + X(OH)'''_n$ can exist in solution, but the molecule:

$$\begin{matrix} Ca = X^{++} & X(OH)''_n \\ \| & + \| \\ H_2 = X^{++} & X(OH)''_n \end{matrix}$$

splits off $H_2XX(OH)_n$ which is the insoluble free globulin and two residual halves, derived from molecules which have decomposed in this manner, unite to yield the calcium globulinate, represented in schematic formulae (2), which is neutral to phenolphthalein:

The same assumption obviously accounts for the fact that the combining capacity of globulin for the alkalies at neutrality to phenolphthalein is twice as great as it is when the alkali in solution its maximum capacity of globulin.

Assuming that the value of ρ for the globulinates of the alkaline earths is 1, while for those of the alkalies it is 2 (corresponding with any of the above pairs of schematic formulae), then the values of $v_1 + v_2$ at 30° for the above globulinates would be:

For potassium globulinate	26.5×10^{-5}
For calcium globulinate	24.4×10^{-5}
For barium globulinate	24.3×10^{-5}
For strontium globulinate	28.5×10^{-5}

Hardy has shown, by direct observation[1] that the specific velocity, per volt per cm potential gradient, of the globulin

[1] W. B. Hardy: Loc. cit.

ion at 18° lies between 10×10^{-5} and 20×10^{-5} cm sec. Increasing these values by 2.7 percent per degree centigrade rise in temperature (which, according to the same observer, is the temperature coefficient of the conductivity of globulinates) at 30° they become, respectively 13×10^{-5} and 26×10^{-5}. The above results, therefore, point to the lower value as being, more probably, the correct one.

Calculating, on the assumption that $\rho = 2$, the values of G, the dissociation constant for these globulinates at 30° we obtain:

Salt	G
Potassium globulinate	0.01470
Calcium globulinate	0.00360
Barium globulinate	0.00493
Strontium globulinate	0.00211

As in the case of the caseinates, the dissociation-constants of the globulinates of the alkaline earths are considerably smaller than those of the globulinates of the alkalies—this is not improbably connected with the greater size of the molecules of the protein salts of the alkaline earths.

Conclusions

(1) The serum-globulinates of the alkalies, in solutions neutral to phenolphthalein (1 gram globulin = 20×10^{-5} equivalents of base), obey Ostwald's dilution-law for a binary electrolyte.

(2) The serum-globulinates of the alkaline earths, in solutions neutral to phenolphthalein, also obey Ostwald's dilution-law for a binary electrolyte.

(3) The value of $\rho(v_1 + v_2)$ where ρ is the number of equivalent gram-molecules of globulinate which is formed by one equivalent gram-molecule of base, and v_1 and v_2 are ionic velocities of the globulinate ions, in cm sec. per potential gradient of 1 volt per cm, is twice as great for the globulinates

of the alkalies as it is for the globulinates of the alkaline earths.

(4) It is concluded that at neutrality to phenolphthalein the globulinates of the alkalies and alkaline earths dissociate into two protein ions, each possessed of twice as many valencies as there are molecules of base bound up in one molecule of globulinate.

(5) On the basis of this conclusion the values of $v_1 + v_2$ (sum of the ionic migration-velocities, or molecular conductivity at infinite dilution) and those of the dissociation-constant are computed for the various globulinates at 30°.

(6) It is probable that at neutrality to phenolphthalein each molecule of globulinate contains two atoms of base, the globulinate of an alkaline earth containing two molecules of globulin linked together, and that the molecule so formed dissociate, in solution, into two quadrivalent *protein* ions, in one of which the metal is bound up in a non-dissociable form. When an alkali is combined with the greatest amount of globulin which it can hold in solution, the globulin neutralizes only half the amount of the alkali which it will neutralize at neutrality to phenolphthalein. In such solutions, therefore, the molecule of globulinate probably contains only one atom of base.

STUDIES IN THE ELECTROCHEMISTRY OF THE PROTEINS. V. THE ELECTROCHEMICAL EQUIVALENT OF CASEIN AND ITS RELATION TO THE COMBINING—AND—MOLECULAR—WEIGHTS OF CASEIN

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I. Introduction

If a direct current of about 1 milliampere be passed through a solution of potassium caseinate, which is neutral to litmus, gas is observed to be evolved at both electrodes, but a firm white spongy precipitate is deposited upon the anode, the cellular texture of which is attributable to entangled bubbles of gas, presumably oxygen.

A quantity of this precipitate was collected in the course of the experiments described below. The anode consisted of a spiral of platinum wire some 9 cm long. This wire, when coated with the precipitate, was well washed in a stream of distilled water, and the precipitate was then scraped off into 99.8 percent alcohol. The precipitate, although firmly adhering to the wire, could readily be separated from it by merely passing the wire through the jaws of a pair of forceps held moderately firmly in the hand. The precipitate which was thus collected under alcohol was washed with alcohol and ether and dried at 30° over H_2SO_4 for 48 hours.

The precipitate proved to be uncombined (base-free) casein. In fact so nearly was it devoid of mineral content as to practically realize that elusive ideal, the "ash-free protein," for one gram of the precipitate yielded less than 2 milligrams of ash. Yet this casein, in every way in which it was tested, proved to be perfectly normal. One gram of the substance, dissolved in 100 cc. of N/10 KOH, increased

the refractive index of the solvent by 0.00155 ±0.00010,[1] while one gram, dissolved in 25 cc. of N/10 KOH and titrated to neutrality to phenolphthalein with N/10 HCl, neutralized 8.3 cc of N/10 KOH.[2]

The possibility was thus indicated of estimating the electrochemical equivalent of casein. Accordingly, the following experiments were undertaken:

II. Experimental

The casein which was employed in these experiments was prepared from Eimer & Amend C. P. Casein "nach Hammersten," further purified by methods described in Part I of these studies.[3]

The caseinate solutions were placed in a U-tube of about 30 cc capacity, 25 cc of solution being employed in each experiment. The anode consisted of a spiral of platinum wire about 0.5 mm thick and 9 cm long, the diameter of the spiral being about 1.2 cm and the "pitch" about 45°. The cathode simply consisted of a platinum wire dipped in the fluid in the outer arm of the U-tube. The U-tube was provided at the bottom with a 3-way stop-cock, which could either be turned so as to provide fluid communication between the two arms of the tube, or else so as to permit the contents of the anodal limb to escape into a receptacle. In this way it was possible to investigate separately, if desired, the contents of each arm of the U-tube. It was found that after electrolysis the fluid in the anodal arm, in which the deposi-

[1] Addition of 1 percent casein changes the refractive indices of aqueous solvents by 0.00152. T. Brailsford Robertson: Jour. Phys. Chem., 13, 469 (1909).

[2] One gram of casein neutralizes about 8.0 cc of N/10 alkali to phenolphthalein. Soldner, Landw. Versuchsstat., 35, 351 (1888), quoted after Van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905); Courant: Arch. f. d. ges. Physiol., 1, 109 (1891); L. de Jager: Nederl. Tijdscher. v. Geneesk, 2, 253 (1897); quoted from Jahresber. f. Thierchem., 27, 276 (1897); H. Timpe: Arch. f. Hyg., 18, 1 (1893); quoted after Raudnitz: Ergeb. d. Physiol., 2, 1, 193 (1903): Laqueur and Sackur: Beitr. z. chem. Physiol. u. Path., 3, 193 (1902): Van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905).

[3] T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

tion of casein occurred, was practically unaltered in reaction although its casein content was much diminished. In the cathodal arm, not only did the casein content diminish, but the alkalinity of the fluid was markedly increased.

The current was led from the terminals of the University 110-volt circuit through a 16 c. p. lamp, a milliamperemeter, a silver titration-voltameter containing 30 cc of N/100 $AgNO_3$, and through the solution of caseinate.

The silver was determined by titration with N/100 ammonium thiocyanate in the presence of a constant excess of nitric acid, a constant quantity. (= 5 cc of a saturated solution) of ferric alum being employed as indicator.

The amount of casein which had been precipitated by the current was estimated by determining the refractive indices of the original and of the electrolyzed solutions at the same temperature; the difference between the refractive indices divided by 0.00152 yields the decrease in the *percentage* of casein contained in the solution consequent upon electrolysis.[1] The quantity of solution employed was always 25 cc. Hence the decrease in the percentage-content of casein, divided by 4, was the amount of casein precipitated by the current.

The experiments were all conducted at 30°.

Varying amounts of casein were dissolved in 100 cc each of KOH solutions of varying concentration so that the proportion of base to casein = 50×10^{-5} equivalents per gram (neutral to litmus)[2] or 80×10^{-5} equivalents per gram (neutral to phenolphthalein) or 100×10^{-4} equivalents per gram.

In estimating the current employed, the electrochemical equivalent of silver, in grams per coulomb, is taken as 0.001118.[3]

It was found that solutions containing a higher proportion of base yielded an apparently lower electrochemical

[1] T. Brailsford Robertson: Jour. Phys. Chem., 13, 469 (1909).

[2] Cf. references in the introduction; also T. Brailsford Robertson: Ibid., 14, 528 (1910).

[3] Guthe: Bull. Bureau of Standards 1905, i, 3, p. 362.

Current employed for precipitation	Solution	Loss after two hours
1 milliamp.	3 percent casein in 50×10^{-5} equivalents KOH per gram	11 milligrams
1 milliamp.	3 percent casein in 80×10^{-5} equivalents KOH per gram	54 milligrams
2 milliamp.	3 percent casein in 80×10^{-5} equivalents KOH per gram	59 milligrams
1 milliamp.	3 percent casein in 100×10^{-5} equivalents KOH per gram	97 milligrams

equivalent for the casein. This was speedily traced to *resolution* of the casein from the electrode after precipitation. The anode, after having been coated with casein by the action of a current of 1 milliampere passing through a 3 percent solution of casein, neutral to litmus, was washed in water, alcohol and ether, dried and weighed. It was then immersed in a solution of casein (3 percent), neutral to litmus, for 2 hours, then withdrawn and washed, dried and weighed as before. It was found to have lost 11 milligrams in weight. Similar experiments were conducted in which the solutions in which the coated wire was immersed were neutral to phenolphthalein and alkaline to phenolphthalein. The foregoing were the results obtained.

Hence doubling the rate of deposition makes very little, if any, difference to the rate of resolution of the casein, but increasing alkalinity of the solution in which the deposition occurs increases the rate of resolution very markedly.[1]

Assuming the rate of resolution to be constant since the contents of the anodic arm are inappreciably altered in reaction in the electrolysis, it is possible to calculate from the above data for each of the solutions and periods employed the loss due to resolution. In the column headed "loss due to resolution" in the accompanying tables these quantities are given; on adding them to the amounts of casein lost from the solution, from which the "apparent" values of the electrochemical equivalent are estimated, one obtains the "corrected" values.

The possible error in the refractometer reading is 1′ of the angle of total reflection; this corresponds to an error of 0.00010 in the refractive index, that is, to an error of 0.07

[1] If the anode be much less than 9 cm in length there is a tendency, after prolonged electrolysis, to what may be termed "floeculent deposition," or precipitation of the casein within the body of the fluid in the anodal arm and not upon the wire. Under these conditions resolution is apparently more rapid and even if the floeculent deposit be filtered off from the anodal fluid before the alkaline cathodal fluid is mixed with it, the values of the electro-chemical equivalent which are obtained are low. No such phenomenon was observed when the anode was of sufficient length.

TABLE I

50×10^{-6} Equivalents of KOH per gram of casein

Percent of casein	Current in amperes	Time of passage	Grams casein lost from solution	Apparent electrochemical in grams per coulomb	Loss due to resolution, milligrams	Corrected electrochemical equivalent
6	11.51×10^{-4}	2 hrs. 15 min.	0.2155 ± 0.0175	0.0231 ± 0.0019	12	0.0244 ± 0.0019
4	9.47×10^{-4}	2 hrs. 0 min.	0.1645 ± 0.0175	0.0241 ± 0.0026	11	0.0257 ± 0.0026
4	18.05×10^{-4}	2 hrs. 15 min.	0.3815 ± 0.0175	0.0261 ± 0.0012	12	0.0269 ± 0.0012
3	10.54×10^{-4}	2 hrs. 0 min.	0.1810 ± 0.0175	0.0238 ± 0.0023	11	0.0253 ± 0.0023
3	17.36×10^{-4}	2 hrs. 0 min.	0.3125 ± 0.0175	0.0250 ± 0.0014	11	0.0259 ± 0.0014
2	11.22×10^{-4}	2 hrs. 0 min.	0.1810 ± 0.0175	0.0224 ± 0.0022	11	0.0238 ± 0.0022
2	15.84×10^{-4}	1 hr. 25 min.	0.1678 ± 0.0175	0.0208 ± 0.0022	9	0.0219 ± 0.0022
					Av.	0.0248 ± 0.0020

TABLE II

80×10^{-5} Equivalents of KOH per gram of casein

Percent of casein	Current in amperes	Time of passage	Grams casein lost from solution	Apparent electro-chemical equivalent in grams per coulomb	Loss due to resolution, milligrams	Corrected electro-chemical equivalent
3.75	10.82×10^{-4}	2 hours	0.1480 ± 0.0175	0.0190 ± 0.0022	54	0.0259 ± 0.0022
3.75	16.03×10^{-4}	2 hours	0.1973 ± 0.0175	0.0171 ± 0.0015	59	0.0222 ± 0.0015
3.75	8.01×10^{-4}	4 hours	0.1810 ± 0.0175	0.0157 ± 0.0015	108	0.0250 ± 0.0015
3.75	8.74×10^{-4}	4 hours	0.2468 ± 0.0175	0.0196 ± 0.0014	108	0.0282 ± 0.0014
3.75	18.31×10^{-4}	2 hours	0.1973 ± 0.0175	0.0150 ± 0.0013	59	0.0194 ± 0.0013
3.75	10.56×10^{-4}	2 hours	0.1052 ± 0.0175	0.0138 ± 0.0023	54	0.0209 ± 0.0023
3.75	19.50×10^{-4}	1 hour	0.1315 ± 0.0175	0.0189 ± 0.0025	30	0.0230 ± 0.0025
					Average,	0.0235 ± 0.0018

TABLE III

100×10^{-5} Equivalents of KOH per gram of casein

Percent of casein	Current in amperes	Time of passage	Grams casein lost from solution	Apparent electro-chemical equivalent in grams per coulomb	Loss due to resolution, milligrams	Corrected electro-chemical equivalent
3	12.03×10^{-4}	2 hours	0.0988 ± 0.0175	0.0114 ± 0.0020	97	0.0226 ± 0.0020
2	12.56×10^{-4}	1 hour	0.0493 ± 0.0175	0.0109 ± 0.0039	49	0.0217 ± 0.0039
					Average,	0.0222 ± 0.0030

in the estimated decrease in the percentage of casein due to electrolysis of the solution, and to an error of 0.0175 in the estimate of the amount of casein deposited by the current. The possible error in each estimate of the electrochemical equivalent, arising from this source, is indicated in the tabulated results.

III. Theoretical

(I) The Valency of Casein Ions.—These average values are obviously, within the experimental error, identical. Now in solutions containing 50×10^{-5} equivalents of base per gram the combining capacity of casein is 50×10^{-5} equivalents per gram, in solutions containing 80×10^{-5} equivalents per gram it is 80×10^{-5} equivalents per gram and in solutions containing 100×10^{-5} equivalents per gram it is between 99 and $10^5 \times 10^{-5}$ equivalents per gram.[1] In the solutions investigated therefore, the combining weight of casein varies 100 percent yet the electrochemical equivalent remains the same.

This fact is probably to be interpreted as follows: I have elsewhere shown[2] that the caseinates of the bases dissociate into two protein ions, in one of which, the cation, the base is bound in a non-dissociable form. On electrolyzing a solution of potassium caseinate, therefore, the anion, free from potassium, would migrate to the anode. There it may be presumed to react with water, liberating oxygen and free casein which combines with the excess of base until the proportion of base to casein in the film in immediate contact with the anode falls to that which obtains at "saturation" of the base with casein. Any additional casein, thus migrating into the film in contact with the anode, must be precipitated as uncombined casein. The cations, containing the potassium, migrate to the cathode and there react with water, liberating KOH, casein and hydrogen, the casein reacting with the excess of KOH to again form potas-

[1] References in Introduction. Also T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

[2] T. Brailsford Robertson: Ibid., 14, 601 (1910).

sium caseinate and to again participate in carrying the current in each direction.

Hence the electrochemical equivalent which is actually measured must in solutions of all reactions be that of casein at "saturation" of the base with the protein.

Rejecting the data obtained in the solutions *alkaline* to phenolphthalein, on account of the possible error arising from hydrolyisis, the average of all the determinations yields the value 0.0242 ± 0.0019 for the electrochemical equivalent of casein. Multiplying this by the Faraday constant, 96530, we obtain the weight of casein in grams which transports one atomic charge. This is 2336 ± 183.

Now at "saturation" of a base by casein the proportion of base to casein is 11.4×10^{-5} equivalents per gram.[1] Corresponding, if, at this reaction, casein combines with only one molecule of base, with a molecular weight of 8772. The *sum of the valencies* of the casein anions must therefore be, on this assumption, $\frac{8772}{2336 \pm 183} = 3.8 \pm 0.3$ or, in round numbers, 4.

If we assume that at "saturation" of the base with casein two, three or four, etc., molecules of base are bound up in one molecule of caseinate the molecular weight of the casein would be, three, or four, etc., times 8772 and the sum of the valencies of the casein anions would be a corresponding multiple of 4. I have elsewhere shown[2] from the depression of the freezing point of water which results from the solution of caseinates therein and from conductivity data that the sum of the valencies of the casein anions or cations in solutions neutral to phenolphthalein must be 4. Hence the data obtained from very different lines of inquiry yield concordant results.

(II) The Relationship of the Salts which are Formed at Saturation of a Base with Casein, to Those which are Formed

[1] T. Brailsford Robertson: Jour. Phys. Chem., 13, 469 (1909); 14, 538 (1910).

[2] T. Brailsford Robertson: Ibid., 14, 601 (1910).

at Neutrality to Litmus and to Phenolphthalein.—Since, at neutrality to phenolphthalein the molecule of caseinate contains 2 atoms of base, the average molecular weight of the salts contained in the solution must be 2500, for at this reaction 80×10^{-5} equivalents of base are bound by one gram of casein.

This would appear to indicate the mixture of a mol. wt. about 2200 with a small proportion of a molecular weight of about 4400. In other words, of:

$$K_2X^{++++} + X(OH)_n''''$$

with a small proportion of:

$$\begin{array}{ccc} KHX^{++} & & X(OH)_n'' \\ \| & + & \| \\ KHX^{++} & & X(OH)_n'' \end{array}$$

In solutions neutral to litmus the salts of casein must possess an average molecular weight which is a multiple of 2000, since at this reaction 50×10^{-5} equivalents of base are bound by one gram of casein. Assuming that at this reaction, also, two atoms of base are bound by one molecule of casein these figures indicate an admixture of:

$$\begin{array}{ccc} KHX^{++} & & X(OH)_n'' \\ \| & + & \| \\ KHX^{++} & & X(OH)_n'' \end{array}$$

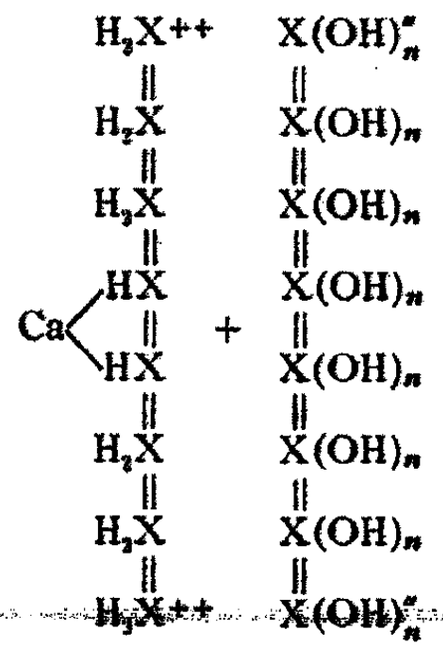
with a small proportion of

$$K_2X^{++++} + X(OH)_n''''.$$

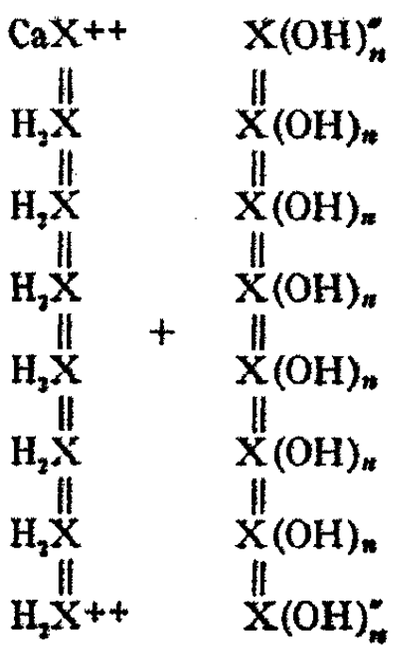
At "saturation" of the base potassium with casein we must have:

$$\begin{array}{ccc} KHX^{++} & & X(OH)_n'' \\ \| & & \| \\ H_2X & & X(OH)_n \\ \| & + & \| \\ H_2X & & X(OH)_n \\ \| & & \| \\ H_2X^{++} & & X(OH)_n'' \end{array}$$

While the corresponding calcium salt would be:



Or:



In the analogous cases afforded by the globulinates this latter salt is not stable, and hence bases *dissolve* globulin in molecular and not equivalent-molecular proportions although at neutrality to phenolphthalein they are bound by the globulin in *equivalent-molecular* proportions.[1]

It appeared of importance to ascertain whether the same is true for the caseinates or whether, on the contrary, the calcium salt of casein which is depicted above is stable.

It is impossible, so far as I have been able to ascertain,

[1] W. B. Hardy: Jour. Physiol., 33, 251 (1905); T. Brailsford Robertson: Jour. Phys. Chem., 15, 170 (1911).

to determine by any *direct* method the equivalence between casein and the alkaline earths at "saturation" of the alkaline earth with the protein. One cannot proceed by simply stirring excess of casein in the solution of alkaline earth because, after the attainment of neutrality to litmus, the rate of solution is so slow that the attainment of "saturation" of the base would be a matter of years.[1]

Nor can one proceed as in the determination of the "saturation" equivalence between the alkalies and casein, by dissolving the casein in excess of base, neutralizing the base with HCl until some casein is precipitated and then determining the proportion of casein which is held in solution by the unneutralized proportion of the base[2] because the caseinates of the alkaline earths are precipitated by the corresponding chlorides. For example:

Four grams of casein were dissolved in 100 cc of 0.048 *N* Ca(OH), and then 40 cc of N/10 HCl were cautiously delivered into the solution by means of a pipette of which the opening was held below the surface of the fluid, the mixture being rapidly and continuously stirred meanwhile. The total volume was then made up to 200 cc and the mixture filtered through soft filter paper. A similar mixture was made up (the "solvent") containing, however, no casein. The refractive indices of the "solvent" and of the "solution" were determined:

Refractive index of solution	1.33216
Refractive index of solvent	1.33201
Difference	0.00015

Corresponding to the presence, in the solution, of 0.1 percent of casein.[2] The 0.008 equivalents of unneutralized $Ca(OH)_2$, therefore held in solution, under these conditions, only 0.2 gram casein, although, in the absence of $CaCl_2$,

[1] T. Brailsford Robertson: Jour. Phys. Chem., 14, 377 (1910).
[2] T. Brailsford Robertson: *Ibid.*, 13, 469 (1909).

0.0008 equivalent of $Ca(OH)_2$ will readily dissolve 1 gram of casein, rendering the solution neutral to phenolphthalein.

In order to determine the equivalence between calcium and casein at "saturation" of the base with casein, therefore, an indirect method had to be devised.

I have elsewhere shown that[1] when casein (concentration C percent) is dissolved in solutions of the hydroxides of the alkalies of varying alkalinity (equivalent-molecular concentration of base $\equiv b_1$) the depression in the conductivity of the solution which is brought about by the addition of the casein ($\equiv \lambda$) is connected with its concentration and with the concentration of the base by the formula:

$$\lambda \times 10^5 = \alpha b_1 - \frac{\beta}{c} b^2 - \gamma c.$$

Where α, β and γ are constants such that when $\lambda \equiv 0$ the value of b_1 is that which would be just sufficient to hold the concentration c of casein in solution (=, for the alkalies, 11.4×10^{-5} equivalents per gram).

I therefore proceeded to ascertain whether the same law holds good for solutions of casein in $Ca(OH)_2$ of varying concentration.

In 400 cc of 0.024 N $Ca(OH)_2$ were dissolved 12 grams of casein, thus making a 3 percent solution neutral to phenolphthalein. To 50 cc portions of this solution were added 0, 2, 4, 6, 8 or 12 cc of 0.048 N $Ca(OH)_2$ and each mixture was diluted to a total volume of 100 cc. The percentage of casein in each of the solutions was therefore 1.5. Exactly similar solutions were made up ("solvents") containing, however, no casein. The conductivities of these solutions were measured in a vessel of resistance capacity 0.1949, at 30° C. The technique employed was the same as that described in Part I of these "studies."[1] The difference between the conductivity, in reciprocal ohms, of the solvent and that of the solution is λ, the depression in conductivity due to the presence of the casein.

[1] T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

The following were the results obtained:

TABLE IV

$b_1 \equiv$ equivalent molecular concentration of $Ca(OH)_2$ in solvent $\times 10^4$	$x_1 \equiv$ the conductivity in reciprocal ohms of the solvent $\times 10^5$	$x \equiv$ the conductivity in reciprocal ohms of the solution $\times 10^5$	$\lambda \times 10^5 = (x_1 - x) \times 10^5$
120.0	263.4	17.1	246.3
129.6	286.6	19.7	266.9
139.2	305.5	23.7	281.8
148.8	325.4	27.9	297.5
158.4	345.0	32.4	312.6
177.6	382.2	41.8	340.4

Applying the above equation to these results and computing the constants from the first, fourth and sixth determinations[1] we obtain:

$$\lambda \times 10^5 = 30830\, b_1 - 488000\, b_1^2 - 53.4$$

Inserting in this equation the above values of b, and computing the corresponding "theoretical" values of, we obtain:

TABLE V

$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Theoretical
246.3	246.3
266.9	264.2
281.8	281.1
297.5	297.5
312.6	312.5
340.4	340.4

It is evident that the relation holds good, also, for solutions of casein in solutions of the hydroxides of the alkaline earths. Computing, from the numerical values of the constants, the value of b_1 when $\lambda = 0$ we obtain:

$$b_1 = 0.031585 \pm 0.029803.$$

[1] These results do not lend themselves to determination of the constants by Gausse's method of solution by least squares, since the normal equations are very nearly identical, the factors differing only by magnitudes commensurate with the experimental error.

Taking the smaller value[1]

$$b_1 = 0.001782,$$

dividing this by 1.5, the percentage of casein, we find $\lambda = 0$ when the equivalence between the casein and the calcium hydroxide is: 1 gram = 11.9×10^{-5} equivalents, a value so near to that (11.4×10^{-5}) obtained for the alkalies that they may be regarded as being, within the experimental error, identical.

Hence it appears that the bases dissolve casein in *equivalent-molecular* not *molecular* proportions, or in other words, that the calcium salt of casein which corresponds to the potassium salt at "saturation" of the base by casein is stable and does not break down into a molecule of salt and a molecule of uncombined protein as the corresponding salt of globulin does.

(*III*) *The Two Possible Types of Salts of the Proteins with Alkaline-earth Bases.*—We have seen that the caseinate of calcium at saturation of the base with casein may be represented by either of the schematic formulae (1):

$$\begin{array}{lcl} H_2X & & X(OH)_n' \\ \| & & \| \\ H_2X & & X(OH)_n \\ \| & & \| \\ HX & & X(OH)_n \\ \| & & \| \\ Ca\langle & + & \| \\ \| & & X(OH)_n \\ HX & & \| \\ \| & & X(OH)_n \\ H_2X & & \| \\ \| & & X(OH)_n \\ H_2X & & \| \\ \| & & X(OH)_n \\ H_2X & & \| \\ & & X(OH)_n' \end{array}$$

or (2)

[1] The larger value probably merely indicates that the effect of small amounts of added casein upon the conductivity of a very alkaline solution is negligible. Cf. T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

$$\begin{array}{ccc} CaX^{++} & & X(OH)_n^{\cdot} \\ \| & & \| \\ H_2X & & X(OH)_n \\ \| & & \| \\ H_2X & & X(OH)_n \\ \| & & \| \\ H_2X & + & X(OH)_n \\ \| & & \| \\ H_2X & & X(OH)_n \\ \| & & \| \\ H_2X & & X(OH)_n \\ \| & & \| \\ H_2X^{++} & & X(OH)_n^{\cdot} \end{array}$$

It would appear probable that the stability and solubility of a molecule of the second type would be very different from those of a molecule of the first type. It is possible that the difference between the behavior of the caseinates and of the globulinates of the alkaline earths at "saturation" of the base with protein is due to the formation of a salt of the first type by casein and of a salt of the second type by globulin, the latter splitting across the middle, setting free a molecule of soluble calcium globulinate.

The possibility may also be indicated that the difference in physical behavior between the *caseinate* and the *paracaseinate* of calcium produced from the caseinate through the agency of rennet may be due to a transformation of salts of the first type into salts of the second type, since paracasein, freed from its combination with calcium, differs in no respect from casein.[1]

(*IV*) *The Relationship between the Combining Capacities of Casein and the Amino-acid Content of the Casein Molecule.*—We have seen that at neutrality to phenolphthalein and to litmus the caseinates in solution may be considered to be mixtures of two salts in forming which the molecular weight of the casein is, respectively, about 2200 and 4400, while at "saturation" of the base with casein the molecular

[1] Van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905).

weight of the combined casein is probably about 8800. It remains to be considered what relation these "theoretical" molecular weights bear to the actual minimum weight of the casein molecule, as indicated by its amino-acid content.

The amino acids which admit of most precise determination are glutamic acid and tyrosin. According to Abderhalden and Rona[1] the percentage of glutamic acid in casein derived from cow's milk is 11.0, indicating a minimum molecular weight, for casein, of 1336, which, multiplied by 3, yields 4008.

The percentage of tyrosin in casein derived from cow's milk is, according to the same authors, 4.5, indicating a minimum molecular weight, for casein, of 4022.

From the percentage of sulphur and phosphorus in casein we similarly deduce a minimum molecular weight approximating to 4000.

The minimum molecular weight of casein, as indicated by the above data, therefore agrees excellently with the molecular weights of casein, deduced from electrochemical data, when in solutions neutral to litmus (4400) or "saturated" with casein (8800) but it is almost twice the weight which we have deduced from electrochemical data for the greater proportion of the casein salts in solutions neutral to phenolphthalein, on the assumption that in such solutions one molecule of casein binds two molecules of base.

Since the depression of the freezing-point of water, which is observed in solutions of caseinates of the alkalies which are neutral to phenolphthalein, is exactly equal to that of a solution of the same molecular plus ionic concentration of the neutralized base, each molecule of the neutralized base must, at least, give rise to one ion of caseinate. If, therefore, we assume the true molecular weight of casein, in these solutions, to be 4400, we must assume that *four* molecules of base are bound in one molecule of the caseinate and that each molecule of caseinate gives rise, in solution, to *four*

[1] E. Abderhalden and P. Rona: Zeit. physiol. Chem., 41, 278 (1904).

ions. Yet these solutions obey Ostwald's dilution law for a *binary* electrolyte.

Without endeavoring to definitely reconcile this discrepancy the tentative suggestions may be advanced that the greater part of the caseinate, in solutions neutral to phenolphthalein, dissociates into two positive and two negative ions.[1] Assuming the possibility of free interaction between all of these ions such a system would behave like a mixture of two salts in constant proportions and would obey Ostwald's dilution law for a binary electrolyte.

Conclusions

(1) If a direct current of about 1 milliampere be passed through a solution of potassium caseinate (neutral to litmus or to phenolphthalein), gas is observed to be evolved at both electrodes, but a firm white spongy precipitate is deposited upon the anode, the cellular texture of which is attributable to entangled bubbles of gas, presumably oxygen. This deposit is identical with base-free casein.

(2) The electrochemical equivalent of casein, whether in solutions containing 50×10^{-6}, 80×10^{-6} or 100×10^{-6} equivalents of base per gram of casein is 0.0242 ± 0.0019 grams per coulomb.

(3) It is concluded that the casein anion migrates to the anode where it reacts with water, liberating oxygen and free casein, which combines with the excess of base in the film surrounding the anode until the proportion of base to casein in this film falls to that which obtains at "saturation" of the base with casein. Any additional casein thus migrating into the film is precipitated upon the anode in the form of free, uncombined casein.

(4) The weight of casein, in grams, which transports one atomic charge is thus 2336 ± 183.

(5) It is concluded that the sum of the valencies of the

[1] Analogous types of dissociation are encountered in solution of many complex salts, for example $K_4Fe(CN)_6$. Cf. Jones and Bassett: Am. Chem. Jour., 34, 313 (1905).

casein anions, in solutions of base "saturated" with casein, is 4 or a multiple of 4.

(6) Solutions of casein in solutions of $Ca(OH)_2$ of varying concentration obey the law

$$\lambda \times 10^6 = \alpha b_1 - \frac{\beta}{c} b_1^2 - \gamma c,$$

where λ is the depression in the conductivity of the solution of $Ca(OH)_2$ which is brought about by the introduction of the casein, b_1 is the equivalent-molecular concentration of $Ca(OH)_2$ in which the casein is dissolved, c is the percentage of casein introduced and α, β and γ are constants, such that when $\lambda = 0$ the proportion of $Ca(OH)_2$ to casein is 11.9×10^{-5} equivalents per gram.

(7) It is inferred that the alkalies and alkaline earths dissolve casein in equivalent molecular proportions.

(8) The probable modes of formation and dissociation of the various casein salts are discussed in the light of these data.

NEW BOOKS

Radiation, Light and Illumination. *A Series of Lectures delivered at Union College. By Charles Proteus Steinmetz. Compiled and edited by Joseph LeRoy Hayden. 16 × 24 cm; pp. xii + 305. New York: McGraw-Hill Book Company, 1909. Price: $3.00 net.*—The lectures which compose the work are: nature and different forms of radiation; relation of bodies to radiation; physiological effects of radiation; chemical and physical effects of radiation; temperature radiation; luminescence; flames as illuminants; arc lamps and arc lighting; measurement of light and radiation; light flux and distribution; light intensity and illumination; physiological problems of illuminating engineering. It is a pleasure to come across a book like this. The author knows his subject, in fact has made his subject, and one cannot read ten consecutive pages without perceiving the difference between first-hand knowledge and the second-hand knowledge which is all that many of us have on any subject. The book is written primarily for electrical engineers interested in problems of illumination; but most of it is of direct interest to chemists and certainly a great deal of it should appeal to physicists, while the consumer would be benefited by glancing over the last two lectures.

There is only one point on which the author has gone astray. It would have been a great deal better to have pointed out that chemical action is produced only by those rays which are absorbed and not to have laid much stress on the chemical action being some kind of a resonance effect, p. 62. As it is the author has an unnecessarily bad time with silver salts and with ozone, p. 95.

The effect of different sources of light on the apparent color of bodies is brought out very clearly on p. 35.

"As the eye perceives only the resultant of radiation, very different combinations of radiation may give the same impression to the eye, but when blotting out certain radiations, as red and green, in the mercury lamp, those different combinations of radiation may not give the same resultant any more, that is, become of different colors, and inversely, different colors, which differ only by such component radiations as are blotted out by an illuminant, become equal in this illuminant. For instance a mixture of red and blue, as a diluted potassium permanganate solution, appears violet in daylight. In the mercury light it appears blue, as the red is blotted out, and in the light of the incandescent lamp it appears red, as the blue is blotted out.

"I show you here, in the light of an incandescent lamp, two pieces of black velvet. I turn off the incandescent lamp and turn on the mercury lamp, and you see the one piece is blue and the other black. Now I show you two pieces of brownish black cloth in the mercury light. Changing to the incandescent lamp you see that the one is a bright crimson, and the other still practically black. In both cases the color deficient in the illuminant appeared as black.

"This tube of copper chloride crystals appears green in the incandescent lamp. In the mercury light it is a dirty white. The excess color, green, is blotted out. These crystals of didymium nitrate, which are a faint light pink in daylight, are dark pink in the incandescent light. In the mercury light they

are blue: the color is a mixture of red and blue, and the one is blotted out in the mercury light and the other in the incandescent light. These two tubes, one containing a concentrated solution of manganese chloride, the other a solution of didymium nitrate, are both a dark pink in the incandescent light. In the mercury light the first becomes a very faint pink, the second becomes grass-green.

"These tubes, one containing a solution of didymium nitrate, the other a diluted solution of nickel sulphate, appear both light green in the mercury light. In the incandescent lamp the former is dark pink, the latter dark green. (Didymium, which formerly was considered as an element, has been resolved into two elements, praseodymium, which gives green salts, and neodymium, which gives pink salts. It is interesting to see that this separation is carried out photometrically by the light: the mercury lamp showing only the green color of the praseodymium, the incandescent lamp the pink color of neodymium.)

"I have here a number of tubes which seen in the light of the incandescent lamp contain red solutions of nearly the same shade. Changing to the mercury lamp you see that they exhibit almost any color. As the red disappeared in the mercury lamp the other component colors, which did not show in the incandescent lamp as they were very much less in intensity than the red, now predominate: potassium permanganate solution turns blue, carmine blue; potassium bichromate greenish brown: coralline (an aniline dye), olive-green; etc., etc.

"Again a number of tubes which in the mercury light appear of the same or nearly the same blue color, turn to a very different color when seen in the incandescent lamp, due to the appearance of red and green, which were not seen with the mercury light.

"A solution of rhodamine, however, which looks a dull red in the light of the incandescent lamp turns a glowing crimson in the mercury lamp, due to its red fluorescence. This diluted solution of rhodamine and methyl green (aniline dyes), which is gray in the light of the incandescent lamp, turns brownish red in the mercury lamp, the green is blotted out while the rhodamine shows its red fluorescence. Thus, you see, the already very difficult problem of judging the subjective colors of bodies under different illuminants is still greatly increased by phenomena as fluorescence.

"To conclude then: we have to distinguish between colorless and colored bodies, between opaque colors and transparent colors, between color, as referred to the visible range of radiation only, or to the total range, including ultra-red and ultra-violet, and especially we have to realize the distinction between objective or actual color, and between subjective or apparent color, when dealing with problems of illuminating engineering."

The bearing of Fechner's law of sensation on photography is discussed on p. 40.

"The result of this law of sensation is that the physiological effect is not proportional to the physical effect, as exerted for instance, on the photographic plate. The range of intensities permissible on the same photographic plate, therefore, is far more restricted. A variation of illumination within the field of vision of 1 to 1000, as between the ground and sky, would not be seriously felt by the eye, that is, not give a very great difference in the sensation. On the photo-

graphic plate, the brighter portions would show 1000 times more effect than the darker portions and thus give halation while the latter are still under-exposed. A photographic plate, therefore, requires much smaller variations of intensity in the field of vision than permissible to the eye. In the same manner the variations of intensity of the voice used in speaking are far beyond the range of impression which the phonograph cylinder can record, and while speaking into the phonograph a more uniform intensity of the voice is required to produce the record, otherwise the lower portions of the speech are not recorded, while at the louder portions the recording point jumps and the voice breaks in the reproduction."

The physiological effects of ultra-violet light are more serious than most of us realize, p. 50.

"Excessive intensity, such as produced at a short-circuiting arc, is harmful to the eye. The human organism has by evolution, by natural selection, developed a protective mechanism against the entrance of radiation of excessive power into the eye: at high intensity of illumination the pupil of the eye contracts and thus reduces the amount of light admitted, and a sudden exposure to excessive radiation causes the eyelids to close. The protective mechanism is automatic; it is, however, responsive mainly to long waves of radiation, to the red and yellow light, but not to the short waves of green, blue and violet light. The reason for this is apparently that all sources of excessive radiation which are found in nature, the sun and the fire, are rich in red and yellow rays, but frequently poor in rays of short wave length, and therefore, a response to short wave lengths alone would not be sufficient for protection as they might be absent in many intense radiations, while a response to long waves would be sufficient since these are always plentiful in the intense radiations found in nature.

"It is only of late years that illuminants, as the mercury lamp, which are deficient in the long waves, have been produced, and for these the protective action of the eye, by contracting the pupil, fails. This absence or reduction of the contraction of the pupil of the eye in the light of the mercury lamp is noticed when passing from a room well illuminated by incandescent lamps to one equally well illuminated by mercury lamps and inversely. When changing from the incandescent light to the mercury light, the illumination given by the latter at first appears dull and inferior as the pupil is still contracted, but gradually gains in intensity as the pupil opens; and inversely, coming from the mercury light to the incandescent light, the latter first appears as a big glare of light, the pupil still being open, but gradually dulls down by the contraction of the pupil.

"This absence of the automatic protective action of the eye against light deficient in long waves is very important, as it means that exposure to excessive intensity of illumination by mercury light may be harmful, due to the power of the light, against which the eye fails to protect, while the same or even greater power or radiation in yellow light would be harmless, as the eye will protect itself against it. The mercury light, therefore, is the safest illuminant, when of that moderate intensity required for good illumination, but becomes harmful when of excessive intensity, as when closely looking at the lamp for considerable time, when operating at excessive current. The possibility of a harmful effect is noticed by the light appearing as glaring. This phenomenon explains

the contradictory statements occasionally regarding the physiological effect of such illuminants.

"Up to and including the green light, no specific effects, that is, effects besides those due to the power of radiation, seem yet to exist. They begin, however, at the wave length of blue light.

"I show you here a fairly intense blue-violet light, that is, light containing only blue and violet radiation. It is derived from a vertical mercury lamp, which is surrounded by two concentric glass cylinders welded together at the bottom. The space between the cylinders is filled with a fairly concentrated solution of potassium permanganate (strong copper nitrate solution or a cupric-ammon salt solution, though not quite so good may be used) which is opaque to all but the blue and violet radiations. As you see, the light has a very weird and uncanny effect, is extremely irritating: you can see by it as the intensity of illumination is fairly high, but you cannot distinguish everything, and especially the lamp is indefinite and hazy: you see by it, but when you look at it, it disappears, and thus your eye is constantly trying to look at it and still never succeeds, which produces an irritating restlessness. It can well be believed that long exposure to such illumination would result in insanity. The cause of this weird effect—which is difficult to describe—is that the sensitive spot on the retina, that is, the point on which we focus the image of the object which we desire to see, or the fova is blue-blind, that is, does not see the blue or violet light. Thus we see the lamp and other objects indistinctly on the outer range of the retina, but what we try to see distinctly disappears when focused on the blue-blind spot. This spot, therefore, is often called the "yellow spot," as we see yellow on it—due to the absence of the vision of blue at this particular place of the retina.

"To produce this effect requires the mercury lamp; most other illuminants do not have sufficient blue and violet rays to give considerable illumination of this color and even if they do, no screen which passes blue and violet is sufficiently opaque to the long waves not to pass enough of them to spoil the effect, if the illuminant is rich in such long waves. The mercury lamp, however, is deficient in these, and thus it is necessary only to blind off the green and yellow rays in order to get the blue and violet light.

"I show you here a mercury lamp enclosed by a screen consisting of a solution of naphthol green (an aniline dye) which transmits only the green light. As you see, in the green the above described effect does not exist, but the vision is clear, distinct, and restful.

"Beyond the violet the radiation is no longer visible to the eye as light. There is, however, a faint perception of ultra-violet light in the eye, not as a distinct light, but rather as an indistinct, uncomfortable feeling, some form of dull pain, possibly resulting from fluorescence effects caused by the ultra-violet radiation inside of the eye. With some practice the presence of ultra-violet radiation thus can be noticed by the eye and such light avoided. In the ultra-violet, and possibly to a very slight extent in the violet and even in the blue, a specific harmful effect appears, which probably is of chemical nature, a destruction by chemical dissociation. The effect increases in severity the further we reach into the ultra-violet, and probably becomes a maximum in the range from one to two octaves beyond the violet. These very short ultra-

violet rays are extremely destructive to the eye: exposure even to a moderate intensity of them for a very few minutes produces a severe and painful inflammation, the after-effects of which last for years, and long exposures would probably result in blindness. The chronic effects of this inflammation are similar to the effect observed in blue light: inability or difficulty in fixing objects on the sensitive spot, so that without impairment of the vision on the rest of the retina clear distinction is impaired and reading becomes difficult or impossible, especially in artificial illumination. It appears as if the sensitive spot or the focusing mechanism of the eye were over-irritated and when used, for instance in reading, becomes very rapidly fatigued and the vision begins to blur. If further irritation by ultra-violet light or by attempting to read, etc., is avoided, gradually the rapidity of fatigue decreases, the vision remains distinct for a longer and longer time before it begins to blur and ultimately becomes normal again.

"The inflammation of the eye produced by ultra-violet light appears to be different from that caused by exposure to high-power radiation of no specific effect, as the light of a short circuit of a high-power electric system, or an explosion, etc.

"The main differences are:

"1. The effect of high-power radiation (power burn) appears immediately after exposure, while that of ultra-violet radiation (ultra-violet burn) appears from 6 to 18 hours after exposure.

"2. The external symptoms of inflammation: redness of the eyes and the face, swelling, copious tears, etc., are pronounced in the power burn, but very moderate or even entirely absent in the ultra-violet burn.

"3. Complete recovery from a power burn even in severe cases usually occurs within a few days, leaving no after-affects, while recovery from an ultra-violet burn is extremely slow, taking months or years, and some after-effects, as abnormal sensitivity to radiation of short wave lengths, may be practically permanent.

"The general phenomena of a severe power burn are:

"Temporary blindness immediately after exposure, severe pains in the eyes and the face, redness of eyes and face, swelling, copious tears, etc. These effects increase for a few hours and then decrease, yielding readily to proper treatment; application of ice, cold boric acid solution, etc., and complete recovery occurs within a few days. In chronic cases, as excessive work under artificial illumination, the symptoms appear gradually, but recovery, if no structural changes in the eyes have occurred, is rapid and complete by proper treatment and discontinuance of work under artificial illumination.

"Most artificial light is given by temperature radiation (incandescent lamp, gas and kerosene flame), and therefore its radiation consists of a very small percentage only of visible light (usually less than 1 percent) while most of its energy is in the ultra-red and invisible, and for the same amount of visible radiation or light the total radiated power thus is many times greater than with daylight. Regarding chronic "power burn," artificial light, therefore, is much more harmful than daylight, that is, much more energy enters the eye under incandescent illumination than under more powerful daylight illumination.

"In a severe ultra-violet burn no immediate symptoms are noticeable, except that the light may appear uncomfortable while looking at it. The onset

of the symptoms is from 6 to 18 hours later, that is, usually during the night following the exposure, by severe deep-seated pains in the eyes; the external appearance of inflammation is moderate or absent, the vision is not impaired, but distinction made difficult by the inability to focus the eye on any object. The pains in the eyes and headache yield very slowly; for weeks and even months any attempt of the patient to use the eyes for reading, or otherwise sharply distinguishing objects, lead to blurring of the vision; the letters of the print seem to run around and the eye cannot hold on to them, and severe headache and deep-seated pains in the eyes follow such attempt. Gradually these effects become less; after some months reading for a moderate length of time during daylight is possible, but when continued too long, or in poor light, as in artificial illumination, leads to blurring of the vision and head- or eye-ache. Practically complete recovery occurs only after some years, and even then some care is necessary, as any very severe and extended strain on the eyes temporarily brings back the symptoms. Especially is this the case when looking at a light of short wave length, as the mercury arc; that is, there remains an abnormal sensitivity of the eye to light of short wave lengths, even such light which to the normal eye is perfectly harmless, as the mercury lamp.

"In chronic cases of ultra-violet burn, which may occur when working on unprotected arcs, and especially spark discharges (as in wireless telegraphy), the first symptoms are: occasional headaches, located back of the eyes, that is, pains which may be characterized either as headache or as deep-seated eye-ache. These recur with increasing frequency and severity. At the same time the blurring of the vision begins to be noticeable and the patient finds it more and more difficult to keep the eye focused for any length of time on objects, as the print when reading. These symptoms increase in severity until the patient is obliged to give up the occupation which exposed him to ultra-violet light, and then gradual recovery occurs, as described above, if the damage has not progressed too far.

"In mild cases recovery from power burns may occur in a few hours and complete recovery from mild ultra-violet burns in a few weeks."

Steinmetz agrees with Woodruff that the black color of negroes is essentially a result of protective pigmentation, p. 59.

"The penetration of the radiation of the sunlight into the human body is very gradually reduced by acclimatization, which leads to the formation of a protective layer or pigment, more or less opaque to the light. Such acclimatization may be permanent or temporary. Permanent acclimatization has been evolved during ages by those races which developed in tropical regions, as the negroes. They are protected by a black pigment under the skin, and thereby can stand intensities of solar radiation which would be fatal to white men. A temporary acclimatization results from intermittent exposure to sunlight for gradually increasing periods: tanning, and enables the protected to stand without harmful effects exposure to sunlight which would produce severe sunburn in the unprotected. This acquired protection mostly wears off in a few weeks, but some traces remain even after years.

"A slight protection by pigmentation also exists in white men, and its differences lead to the observed great differences in sensitivity to solar radiation:

blondes, who usually have very light pigmentation, are more suseeptible to sunburn and sunstroke than the more highly pigmented brunette people.

"In sunburn we probably have two separate effects superimposed one upon the other: that due to the energy of the solar radiation and the specific effect of high frequencies, which to a small extent are contained in the sunlight. The two effects are probably somewhat different, and the high-frequency effect tends more to cause inflammation of the tissue, while the energy effect tends toward: the production of pigmentation (tanning) and the symptoms of sunburn thus vary with the different proportions of energy radiation and of high-frequency radiation as depending on altitude, humidity of the air, the season, etc."

The paragraphs on the question of heat luminescence in the Welsbach mantle, p. 91, are of great interest.

"A body, which gives at any frequency a greater intensity of radiation than a black body of the same temperature is called luminescent, that is said to possess 'heat luminescence.' Characteristic of heat luminescence, thus is an excess of the intensity of radiation over that of a black body of the same temperature for some frequency or range of frequencies, and the color of luminescence is that of the radiation frequencies by which the luminescent body exceeds the black body.

"It is not certain whether such heat luminescence exists. The high efficiency of light production of the Welsbach mantle, of the lime light, the magnesium flame. the Nernst lamp, etc., are frequently attributed to heat luminescence.

"The rare oxides of the Welsbach mantle, immersed in the bunsen flame, give an intensity of visible radiation higher than that of the black body, as a graphite rod, immersed in the same flame, and if we assume that these oxides are at the same temperature as the flame in which they are immersed, their light must be heat luminescence and not colored radiation, and the latter cannot exceed that of a black body. It is possible, however, that these oxides are at a higher temperature than the flame surrounding them, and as the radiation intensity of a black body rapidly rises with the temperature, the light radiation of the rare oxides, while greater than that of the flame temperature may still be less than that of a black body of the same temperature which the oxides have, and their radiation, thus, colored temperature radiation and not luminescence. Very porous materials, as platinum sponge, absorb considerable quantities of gases, and by bringing them in close contact with each other in their interior cause chemical reaction between them, where such can occur, and thus heat and a temperature rise above surrounding space. Thus platinum sponge, or fine platinum wire immersed in a mixture of air and alcohol vapor at ordinary temperature, becomes incandescent by absorbing alcohol vapor and air and caus ng them to combine. The oxides of the Welsbach mantle, as produced by the deflagration of their nitrates, are in a very porous state and thus it is quite likely that in the bunsen flame they absorb gas and air and cause them to combine at a fa more rapid rate than in the flame, and thereby rise above the flame temperature. An argument in favor of this hypothesis is that these oxides, when immersed in the bunsen flame in close contact with a good heat conductor, as platinum, and thereby kept from rising above the flame temperature, do

not show this high luminosity. I have here a small fairly closely wound platinum spiral filled with these oxides. Immersing it in the bunsen flame you see the oxides and the platinum wire surrounding them glow with the same yellow light, but see none of the greenish luminosity exhibited by the oxide when free in the flame, except at a few points at which the oxide projects beyond and is not cooled by the platinum spiral. The absence of a high selective luminosity of these oxides, when heated electrically in a vacuum or in an inactive gas, also point this way. The gradual decay of the luminosity shown by such radiators may be due to their becoming less porous, by sintering this would account for the very rapid decay of the light of the lime cylinder in the hydro-oxygen flame, and the very small decay of the more refractive oxides in the Welsbach mantle—but it also may be the general characteristic of luminescence, as we have found in the discussion of fluorescence and phosphorescence.

"In favor of heat luminescence as the cause of very high efficiency of these radiators is, however, the similarity of the conditions under which it occurs, with those we find in fluorescence and phosphorescence. Just as neither calcium sulphide nor zinc silicate nor calcium carbonate are fluorescent or phosphorescent, when chemically pure, but the fluorescence and phosphorescence are due to the presence of a very small quantity of impurities, as manganese, so the pure oxides, thoria, erbia, ceria, do not give very high luminosity in the bunsen flame, but the high luminosity is shown by thoria when containing a very small percentage of other oxides."

The relative merits of some different forms of arc conduction are discussed on p. 122.

"Essentially, however, the efficiency of light production by the arc is a characteristic of the material of the arc stream, and thus substances which give a large part of their radiation as spectrum lines in the visible range—as calcium—give a very efficient arc, while those substances which radiate most of their energy as lines in the invisible, ultra-violet or ultra-red—as carbon—give a very inefficient arc. The problem of efficient light production by the arc therefore consists in selecting such materials which give most of their radiation in the visible range.

"Carbon, which is most generally used for arc terminals, is one of the most inefficient materials: the carbon arc gives very little light, and that of a disagreeable violet color; it is practically non-luminous, and the light given by the carbon arc lamp is essentially incandescent light, temperature radiation of the incandescent tip of the positive carbon. The fairly high efficiency of the carbon arc lamp is due to the very high temperature of the black body radiator, which gives the light.

"The materials, which give the highest efficiencies of light by their spectrum in the arc stream are mercury, calcium, and titanium. As mercury vapor is very poisonous, the mercury arc has to be enclosed air-tight, and has been developed as a vacuum arc, enclosed by a glass or quartz tube. Its color is bluish green. Calcium gives an orange-yellow light of a very high efficiency, and is used in most of the so-called 'flame-carbon arcs,' or 'flame arcs.' Titanium gives a white light of extremely high efficiency. It is used in the so-

called 'luminous arc,' as the magnetite arc in direct current circuits, the titanium-carbide arc in alternating current circuits."

The question of efficiency comes up on p. 126.

"As, by electro-luminescence, electric energy is converted more directly into radiation, without heat as intermediary form of energy, no theoretical limit can be seen to the possible efficiency of light production by the arc, and in the mercury, calcium and titanium arcs, efficiencies have been reached far beyond those possible with temperature radiation. Thus, specific consumptions of 0.25 watt per mean spherical candle power are quite common with powerful titantium or calcium arcs, and even much better values have been observed. It is therefore in this direction that a rapid advance in the efficiency of light production appears most probable. At present, the main disadvantage of light production by the arc is the necessity of an operating mechanism, an arc lamp, which requires some attention, and thereby makes the arc a less convenient illuminant than, for instance, the incandescent lamp, and especially the limitation in the unit of light: the efficiency of the arc decreases with decrease of power consumption and, while the arc is very efficient in units of hundreds or thousands of candle power, its efficiency is much lower in smaller units, and very small units cannot be produced at all. Thus, for instance, while a 500 watt flame arc may give 10 times as much light as a 500 watt carbon arc, to produce by a flame arc the amount of light as given by a 500 watt carbon arc requires very much more than one tenth the power. So far no way can be seen of maintaining the efficiency of the arc down to such small units of light as represented by the 16- or 20-candle power incandescent lamp."

The following paragraph, p. 174, shows that Steinmetz is not a believer in the photometer.

"Light is used for seeing things by, that is distinguishing objects and differences between objects. Regarding this feature, the distinction of objects given by them, different colored lights can be compared, and a green light can be made equal to a red light in illuminating value.

"It thus means that any two lights, regardless of their color, have the same intensity if, at the same distance from them, objects can be seen with the same distinctiveness, as, for instance, print read with equal ease. The only method, therefore, which permits comparing and measuring lights of widely different color is the method of 'reading distances,' as used in the so-called *luminometer*. It after all is the theoretically correct method of comparison, as it compares the lights by that property for which they are used. Curiously enough, the luminometer, although it has the reputation of being crude and unscientific, thus is the only correct light-measuring instrument, and the photometer correct only in so far as it agrees with the luminometer, but, where luminometer and photometer disagree, the photometer is wrong, as it gives a comparison which is different from the one shown by the light in actual use for illumination.

"The relation between luminometer and photometer for measuring light intensity, therefore, is in a way similar to the relation between spark gap and voltmeter when testing the disruptive strength of electrical apparatus: while the voltmeter is frequently used, the exact measure of the disruptive strength is the spark gap and not the voltmeter, and, where the spark gap and voltmeter disagree, the voltmeter must be corrected by the spark gap. In the

same manner the luminometer measures the quality desired—the illuminating value of the light—but the photometer may be used as far as it agrees with the luminometer."

The development of the American city lighting system is given on p. 274.

"In the early days of using arc lamps for American city lighting, lighting towers were frequently used, and such tower lighting has still survived in some cities. One or a number of arc lamps are installed on a high tower and were supposed from there, like artificial suns, to spread their light over an entire city district.

"This method of city lighting was found unsatisfactory, as it did not give enough light. It is unsatisfactory, however, not in principle, but because it was too ambitious a scheme. If, in street illumination, we double the distance between the lamps, each unit must have four times the light flux to get the same minimum density, as the distance is doubled, and the flux density decreases with the square of the distance. At twice the distance between the lamps, each lamp thus must have four times the light flux, and each mile of street thus requires twice the power. Reducing the distance between lamps to half reduces the power to one-half with the same minimum illumination. In street lighting it is therefore of advantage to use as many units of illuminants as possible, and bring them together as close as possible, and correspondingly lower their intensity, up to the point where the increasing cost of taking care of the larger numbers of units and increasing cost of poles and connections compensates for the decreasing cost of energy. There is a minimum which probably is fairly near our present practice.

"When, however, you come to square and exposition lighting, you find that the distance between the illuminants has no effect on the efficiency. Let us assume that we double the distances between the lamps which light up a large area. Then each lamp requires four times the light flux to get the same minimum flux density between the lamps, but at twice the distance between the lamps each lamp illuminates four times the area, and the total power per square mile of lighting a large area, like an exposition, thus is independent of the number of lamps used, and, whether you place them close together or far apart, you require the same total flux of light, and if you keep the same proportions of height from the ground and distance between lamps, you also get the same variation between maximum and minimum intensity. But, supposing the lamps to be placed further apart, the maximum or minimum points also are further apart, and you get a more satisfactory illumination by having a less rapid intensity variation. That points to a conclusion that, for exposition lighting, the most efficient way would be to use a relative moderate number of high-power sources of light on high-towers at distances from each other of the same magnitude as the height of the towers. We would get a greater uniformity and better physiological effect by having the illumination further apart, and they would require the same total light flux, and therefore the same power, as if you bring the lamps close to the ground, and place them very close to each other. The tower lighting therefore is the ideal form for lighting a large area. When the arc was first introduced, it was so much superior to any other illuminant known before, that people vastly overrated it. They thought that they could light the whole city by it, and in trying to do so these towers would have been

the proper way, but very soon it was found that even with the efficiency of the arc, to light not only the streets, but the whole area of the city, would require an entirely impracticable amount of light flux. It thus was too ambitious a scheme for city lighting, but it should be done in exposition work. City illumination thus has come down from this first ambition to light the whole city to an attempt to light only the streets. For the latter purpose, however, lighting towers are inefficient, since much of the light flux is wasted on those places which we no longer attempt to light; in exposition lighting, however, the most effective general illumination would be given by white arcs on high towers, leaving the concentrated or decorative illumination to the incandescent lamp and flame arc, of yellow color."

Most of us believe that diffused lighting is an ideal, though expensive method for interiors; but Steinmetz is by no means dogmatic on this point, p. 279.

"Furthermore, the relations between directed and diffused light have in the illuminating engineering practice been obscured to some extent by the relation between high and low intrinsic brilliancy and between direct and indirect lighting. Thus, to eliminate the objectionable feature of high intrinsic brilliancy of the illuminant, direct lighting by light sources of high brilliancy, which was largely directed lighting, has been replaced by indirect lighting, by reflection from ceilings, etc., which is diffused lighting. Where such change has resulted in a great improvement of the illumination, it frequently has been attributed to the change from direct to diffused lighting, while in reality the improvement may have been due to the elimination of high brilliancy light sources from the field of vision, and engineers thereby led to the mistaken conclusion that perfectly diffused lighting is the preferable form. Again, in other instances such a change from direct to indirect lighting has not resulted in the expected improvement, but the indirect lighting has been found physiologically unsatisfactory, and the conclusion drawn that the elimination of high brilliancy from the field of vision has not been beneficial, while in reality the dissatisfaction with the indirect light was due to the excess of diffused light and absence of directed light, and this improper proportion between directed and diffused light more than lost the advantage gained by eliminating the light sources of high brilliancy from the field of vision. In this case the proper arrangement would have been to reduce the brilliancy of the light sources, by diffusing or diffracting globes, to a sufficiently low value, but leave them in such a position as to give the necessary directed light.

"Thus, in illuminating engineering, as in other sciences, it is very easy to draw erroneous conclusions from experience by attributing the results to a wrong cause. Any changes in the arrangement usually involves other changes: as in the above instance, the change from high to low brilliancy commonly causes a change from directed to diffused light; by attributing the results to the wrong cause, serious mistakes thus may be made in basing further work on the results."

The reviewer would have been glad to have quoted twice as many pages from this extremely interesting book; but it would probably be just as difficult to stop then as now.

Wilder D. Bancroft

La Chimie de la Matière vivante. *By Jacques Duclaux. (Nouvelle Collection scientifique. Directeur: Émile Borel.) 12 × 18 cm; pp. 281. Paris: Félix Alcan, 1910. Price: paper, 3.50 francs.*—The headings of the chapters

are: the law of chemistry; chemical synthesis; notions of symmetry; the function of chlorophyll; the diastases; alcoholic fermentation; organized matter; catalysis; chemical equilibrium chemical infinitesimals; life and death.

The unsuccessful attemps of Cotton to produce optically active substances by the action of circularly polarized light, p. 53, bring up the whole question. "We have been forced to assume the existence in nature of asymmetric forces. What are they? In the vegetable kingdom, all the compounds are formed originally from carbon dioxide and water, both symmetrical substances, under the influence of light which is a symmetrical force. The only place where asymmetry can come from is the seed. The whole vegetable is only a developed seed and it is quite conceivable that the asymmetrical forces existing in the seed, in consequence of the presence of optically active substances, might cause asymmetry during germination or development when they act on carbon dioxide, light and water. That leaves us face to face with the question why the seed should be asymmetric. This is as much of a puzzle as the question whether the hen or the egg came first."

From the author's calculation, p. 71, as to the utilization of the sun's rays by growing crops, he concludes that less than one percent efficiency is obtained. If we could get one hundred percent efficiency we could raise one hundred and fifty pounds of potatoes per square foot, p. 74, which would be intensive farming with a vengeance. While one percent efficiency seems low, we must remember, p. 77, that "in one thousand liters of air there is only one-third of a liter of carbon dioxide and perhaps twenty liters of water vapor. A plant which has to nourish itself on this mixture is in much the same state as the traveler, who should try to drink the water dissolved in the wind of the Sahara."

We usually call a substance a catalytic agent when it can convert a relatively large amount of one substance into another without any appreciable change in its concentration taking place. The author points out, p. 84, that we must be careful in applying such a test because we have a reaction according to the law of definite proportions between carbon tetra-iodide and hydrogen in which one gram of hydrogen converts five hundred and twenty grams of carbon tetra-iodide into hexa-iodo ethane.

On p. 92, we learn that "although our nourishment seems complicated, it is really quite simple since we have only to deal with three classes of food: the carbohydrates (starch, sugar); nitrogenous substances (casein of milk, albuminoids of legumes or of meat) and fats (vegetable oils, animal fats). There are special diastases for each one of these groups. The first, as we have just seen, has amylase and its two acids: the second has pepsine, secreted by the mucous membrane of the stomach, and also the different diastases of the pancreas, among which is trypsine. The third group has lipase.

"All these digestive diastases have one character in common. Under normal conditions their action is one of splitting and they simplify the molecule of the substance on which they act, decomposing them into others which are simpler and more soluble. Glucose is more simple than maltose and dextrine more simple than starch. The peptones, formed by the action of pepsine on nitrogenous foods, have simpler molecules than the foods from which they are formed. Glycerine and the fatty acids are also simpler than the fats from which they are formed by the action of lipase on the fats or oils."

At first sight it seems as though it ought to be easy to crush the cells of yeast so as to obtain the zymase; but the author points out, p. 114, that it is really a very difficult matter because the cells are less than 0.01 mm in diameter and are as elastic as small rubber balls.

The author is in the Pasteur Institute and naturally is anxious to uphold Pasteur's dictum that living matter is essential to fermentation. In the case of Buchner's zymase, p. 115, it is admitted that there are no cells and that "alcoholic fermentation can take place in the absence of any living organism, *in the sense in which we usually use the phrase.*"

The author gets around the difficulty by considering zymase, p. 120, as living matter. "The external membrane of a cell is necessary for the continued existence of the cell, for, if it were not there, the slightest agitation would cause the contents of the cell to mix with the surrounding liquid. It is not however a necessary condition of life, at least for a short time. It encloses and protects the cell but does not constitute it. Buchner's process of extraction is really one of skinning the cell. It takes from the cell its individuality and its defence against the outside world; *but not its life*, and that is why we find the properties of yeast in the juice which has been pressed out. A flask full of this juice is a rudimentary cell. When left to itself, this cell dies like an ordinary cell, *i. e.*, it loses its diastasic properties. It loses them less rapidly if one adds sugar, because sugar is a food for it even in its mutilated state. It still breathes because it gives off carbonic acid spontaneously. Possibly it assimilates because one only finds eighty-five grams of sugar in the form of alcohol and carbonic acid for every hundred grams of sugar supplied. The other fifteen grams have disappeared without leaving a trace, as though they had combined with something. Of course those properties which depend on the structure and form of the cell or on the presence of the nucleus are completely destroyed. One would not expect to see such a giant cell reproduce itself. But, no matter how savage the treatment to which the yeast is subjected during the extraction of the juice, there is nothing in the rapid extraction which would cause a chemical change in the protoplasm of the cell, since the only substances with which it comes in contact are sand and tripoli, both completely inert substances. We thought that we were realizing life without a cell and all that we have done was to change several millions of resisting cells into a single one which is much larger and more delicate. Zymase has not yet been separated from living matter; *it is still to be discovered.*"

To the reviewer the preceding paragraph seems like a case of special pleading; but the author's point of view is certainly an interesting one. The author's idea that starch is an amorphous crystal, p. 134, is also a novel one.

"The structure of the starch molecule enables us to account for its properties fairly readily. We understand, for instance, why starch cannot be obtained in crystals; its molecule is too complex just as we had been led to suppose. We have already seen that a molecule containing six atoms can only form crystals which are almost completely lacking in symmetry. Molecules containing six hundred atoms will form entirely unsymmetrical crystals with irregular piling. This does not mean that the substances are completely *isotropic* like glass (that is, having the same properties in every direction): but merely that the exterior form may be anything. In fact, when we look into the matter more closely,

we find it necessary to modify what I said at first. It is not absolutely accurate to say that organized substances do not crystallize. Many of them do, but in the *amorphous system.*

"This sounds like a joke and calls for an explanation. Crystals are not characterized solely by their external form, by their faces and by the constant angles which the faces make. They are also characterized by their optical properties and especially by the phenomena to be noted when the crystals are examined in polarized light. The crystals, so-called, are not the only substances which show these phenomena. Under certain conditions, certain liquids give the same results. This has caused people to broaden the definition of a crystal considerably and to make it depend much more on the optical properties than on the external form. In addition to the crystalline systems of the mineralogists, we also recognize the amorphous system for all substances which have these properties without having a constant geometrical form. Many of the organized substances, and especially starch, belong in this category for it yields under polarized light results which are very much like those obtained with crystals."

On p. 145, the author calls attention to the act that when colloidal solutions are evaporated to dryness, the solid residue becomes absolutely insoluble. "I am forced to insist on the word 'absolutely' because many chemists have the bad habit of calling substances insoluble when they are not readily soluble: calcium carbonate, for instance, of which a liter of water dissolves three centigrams; barium sulphate or silver chloride which dissolve to the extent of two milligrams in a liter of water. The word 'insoluble' should be kept for colloidal substances which usually dissolve to less than one one-thousandth of a milligram per liter of water. The difference may not appear large if one considers the amount of substance per liter of water; but it becomes more noticeable if one considers that 500 liters of water would dissolve one gram of silver chloride while it would take at least one million liters to dissolve one gram of a colloid.

"This gives us a very simple reason why certain organisms are composed of colloids; insolubility is an absolute essential for existence. We cannot conceive of fishes whose bodies are soluble in water. It is still more difficult to conceive of such a thing in the case of microbes, because their bodies are so very small that they would dissolve instantaneously in water if they were soluble to any extent. The outer membrane of the microbe must resist water indefinitely and to do that it must be absolutely insoluble, for microbes are often in contact with enormous masses of water. In one experiment of Trenkmann's sixteen hundred of the tuberculosis bacilli were kept alive in one centimeter of water although this means that a gram of microbes (dry weight) was suspended in an ocean of ten million liters of water and that the contact surface was ten square meters.

"This necessary insolubility does not by itself prove that the membranes must be colloidal, for the body of a microbe would resist the action of water if the microbe were wrapped in gold-leaf which is not a colloid at all. Even if we ignore the fact that the skin of the microbe must be permeable to water and to certain salts, a condition not fulfilled by gold-leaf, we must remember that the membrane is formed by the microbe. In every case in which an absolutely insoluble substance is formed by a chemical reaction which does not take place too slowly (and that is not the case here), the molecules of the compound unite to form micellae and the compound assumes the colloidal form regardless whether

it remains suspended or whether it appears at once as an amorphous solid. Therefore the membrane, being insoluble and being formed by the microbe, must be a colloid."

On pp. 250–252, we find some suggestive paragraphs—"In a chapter devoted to life and death, a place should be reserved for the intermediate state known as sickness. Death is the final upsetting of all the functions and sickness is a temporary disturbance of them, in other words a chemical or physico-chemical change in some of the functions. It is therefore chemistry which must fight against sickness. This is now being done and the number of remedies increases day by day. Unfortunately progress is made blindly and as the result of luck. If medicine is ever to become a science, we must study and recognize a disease before trying to cure it. We must know the way in which all the organs act, in other words we must know the diastases which are secreted, the equilibria which are maintained, and the reason for everything that happens. The study of these matters is simplified very much by the fact that most of the functions continue after death even when the organ has been removed from the body. This enables us to make a preliminary classification into independent groups. Since each disturbance can be defined and measured by its disappearance or decrease, or by an abnormal increase in some of the functions, it will be relatively easy then to find a remedy.

"To show that all this is possible, I will cite a case where the physiologists have already done half the work. For digestion to take place in the stomach, there must be a diastase present, pepsin, and there must also be a certain amount of free hydrochloric acid. This can be shown by a purely chemical experiment in a test-tube; when there is no acid, the pepsin is inactive. Since dyspepsia is due to an insufficient digestion in the stomach, it seemed plausible to attribute this to a lack of hydrochloric acid. Once this was recognized, it was a very simple matter to help things along by increasing the amount of hydrochloric acid artificially, in other words by taking a few drops of acid with each meal. This is a very good instance of the method which ought to be followed in all cases, through it must be remembered that we have found a palliative and not a remedy. A real cure will not be effected until the mucous membrane of the stomach has recovered the power to secrete sufficient quantities of hydrochloric acid.

"All the functions can be submitted to an examination like that made on the effect of gastric juice on digestion. No matter what the disturbance, chemistry can find a specific remedy as soon as the examination is finished. The examination must be based in the study of the diastases, the catalyses, and the chemical equilibria of which we have recognized the importance in the preceding chapters. Above all it must be based on the study of the colloidal substances which form the greater part of our tissues. This study has been begun along several lines; but, unfortunately, by empirical methods so that it is difficult to interpret the results that have been obtained. We have tried to go too fast and to draw conclusions applicable in medicine and physiology before knowing the exact nature of colloids. It was a bad way to do and the result of it is that the word 'colloid' is considered by many merely as a serviceable one to use when putting out new pharmaceutical products. We

must start in again practically from the beginning, making continuous use of physical chemistry, as that seems to be our only chance of success."

Wilder D. Bancroft

La Stabilité de la Vie. *Étude énergétique de l'Évolution des Espèces. By Félix Le Dantec. (Bibliothèque Scientifique Internationale.) 13 × 22 cm; pp. xii + 300. Paris: Félix Alcan, 1910. Price: bound, 6 francs.*—The book is divided into four parts: biology and physics; the language of energetics; continuous phenomena; vital energy. There is a good deal in the book, to which most people will take exception; and the author is rather given to quibbling, as in the paragraphs on the degradation of energy, page 46. For all that, there are many paragraphs which are of great interest.

On page 11 the author says: "I believe that life has its place among the other natural phenomena, and that biology is only a subdivision of physics. I therefore believe that, in biology as in physics, there are fundamental principles from which can be deduced consequences which are easy to predict. I believe that we may have deductive biology just as much as thermodynamics or mathematical optics. I also believe that this deductive biology will some day play as important a part in the natural sciences as does mathematical physics in physics. We can then make experiments which will mean something, instead of so-called experiments having no aim and no justification, made by investigators unfamiliar with scientific method. We shall then be able to say in regard to certain alleged observations that they are either inaccurate or have not been interpreted properly. If there is no such deductive biology there is no natural *science*. I claim that there is a deductive biology and that many of its principles are known."

On page 14, we find the following paragraph: "My views on the inheritance of acquired characters have not yet been confirmed by any further experimental investigation. I hope to show, without introducing any hypothesis, that such a verification is absolutely unnecessary and that the known biological facts permit us to establish *à priori* and without possibility of error, a law without which evolution would be a meaningless word."

The fundamental principle of the book is summed up as follows on page 20:

1. A living substance is in a state of stable equilibrium.

2. When a living substance undergoes pathological changes which do not cause death, it either returns to the former stable state, in which case there is no specific variation; or it undergoes a specific variation in which case it passes *into a more stable state than the one it has left.*

This is true enough as the author intends it; but it is not happily expressed, and it is not very helpful because it does not show the direction of the change. What the author really means is that a system changes so as to become better adapted to the new conditions. It is of course more stable under those conditions because it no longer tends to change; but the use of the word "stable" is misleading. Unless one knows in what way the system is to change, no use can be made of the author's generalization. If the author had made consistent use of the Theorem of Le Chatelier, page 25, he would have placed his deductive biology on a much firmer foundation.

Wilder D. Bancroft

TEMPERATURE MEASUREMENTS IN AN EXPERIMENTAL CARBORUNDUM FURNACE

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SOCIETE CHIMIQUE BIBLIOTHEQUE DE FRANCE

The following is an account of work done on an experimental carborundum furnace, with special reference to the temperatures attained, the methods of measuring those temperatures, and the calibration of the pyrometers used.

The power available in the preliminary experiments was from the A. C. lighting circuit, giving up to 200 amperes at 110 volts and regulated by a brine rheostat; in the final experiments, that from a G. E. motor generator, consisting of a Form K, Type 1, 60 cycle, 2200 volt, 40 ampere, 150 H. P. induction motor with starting compensator; the motor being directly coupled to a Form A, Class 6, 2000 ampere, 35 volt, 27.4 cycles, 75 H. P. double current generator from which D. C. can be drawn direct, and A. C. through a form B-1, Type 00, 150 H. P. oil transformer. The generator is separately excited by a Form H, Class 2, 125 volt, 26 ampere D. C. generator. By adjustment of the transformer ratios and the field and exciter rheostats any voltage from 0 to 200 may be obtained by steps of about one volt. The voltage was measured on a Thomson double scale voltmeter and the current either on a 500 ampere Weston instrument, or a 2100 ampere Leeds and Northrup mercury ammeter, the latter being set up permanently in series with the furnace. The mercury ammeter is very satisfactory for student use in a university laboratory for such work as the preparation of aluminum, where an accidental short-circuit through the bath, in student hands, may overload and ruin an ordinary ammeter.

For the temperature measurements, there were available: thermocouples; Wanner, Morse and Thwing pyrometers; a Lummer-Brodhun spectrophotometer with rotating sector disk; Weston, and Leeds and Northrup potentiometers; tubes

of carbon, graphite and carborundum composition, etc. These will be described later.

The electrodes were of carbon, from the National Carbon Co., or Acheson graphite, and varied in size from a diameter of $1^3/_{16}''$ in the preliminary runs to $2'' \times 4''$ in the final ones. The square or rectangular electrodes were held in specially designed watercooled electrode holders of Tobin bronze, consisting of a plate $8'' \times 4'' \times {}^7/_8''$ upon which was a box $4'' \times 4'' \times 2''$ high, with ${}^1/_4''$ walls, the box containing two tubes of ${}^1/_4''$ bore, one reaching almost to the bottom of the box and one just passing through the top, to carry the cooling water. Holes were drilled in the projecting parts of the base plates, and by bolting two of these plates around an electrode, we can offer 16 sq. in. of cooling surface on two sides of the electrode. These holders were very efficient. We have run under such an overload that the electrodes would be red hot within an inch of the holder, and with a full stream of cooling water, the electrode between the two parts of the holder would not be too hot to handle. The holders insured very good electrode contacts.[1]

The furnaces were built up of Queen's Run firebrick, loosely laid together. The walls were in all cases 4" thick, the width of a brick. The furnaces varied in size from about 12" to 20" long, 12" wide and 12" high, inside dimensions, taking 15 to 25 kw in the preliminary runs, to 27" long and the cross-section dimensions shown in Fig. 1, taking up to 50 kw and using about 150 pounds of charge, in the final runs.

The small circles in Fig. 1 represent gas pipe supports running underneath three layers of the brick. Using this form instead of a rectangular one, we do away with the waste space in the corners and hence have much less unchanged charge at the end of the run. The Niagara furnaces as now built are of an approximately circular cross-section, the curved

[1] These holders may be obtained from Champaign Bros., Ithaca, N. Y., at a cost of less than $20.00 for a complete set of four pieces.

side walls being made in movable sections of firebrick set in iron frames.[1] In the old rectangular furnaces there was considerable unchanged charge, which was worked up into the next charge [2, p. 38]. In the present form of furnaces almost no unchanged charge is obtained, and what little there is is used in the silicon furnaces instead of being worked up into other carborundum charges. H. N. Potter[3] has also used it in the manufacture of silicon monoxide.

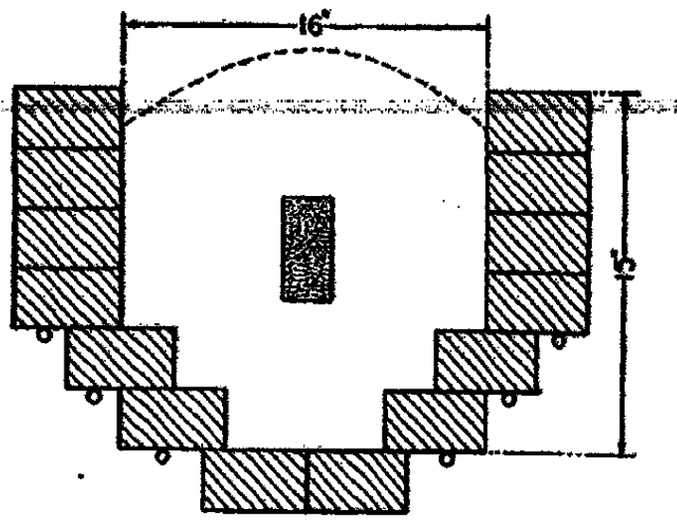

Fig. 1.—Cross-section of furnace.

The electrodes in the furnace shown in Fig. 1 were of carbon, 2″ × 4″ (made up of two 2″ × 2″) and projected through the furnace walls $5^1/_2$″, this distance being sufficient to prevent slagging of the brick walls. Between these was built a core 2″ wide, 4″ high and 16″ long, consisting of granular (crushed) carbon from the National Carbon Co. This carbon all passed a sieve of 3 meshes to the inch, 55 percent remained on a 6-mesh sieve, 54 percent on a 12-mesh, and only 1 percent passed the 12-mesh.

The raw materials for the charge were white sand or crushed quartz, obtained through the kindness of Mr. F. J. Tone, of the Carborundum Co., analyzing 99.4 percent SiO_2, 0.4 percent residue from HF treatment, 0.2 percent loss on ignition; coke analyzing 83 percent fixed carbon, 10 percent

[1] These figures refer to the bibliography at the end of this paper.

ash, 3 percent moisture, and 4 percent volatile; sawdust analyzing 38 percent carbon; and commercial salt.

The normal charge was as follows:

Parts by weight	
53.5	Sand
40.0	Coke, ground to pass a 14-mesh sieve
5.0	Sawdust
1.5	NaCl

The equation $SiO_2 + 3C = 2CO + SiC$ requires 36 parts carbon for each molecular equivalent, 60.4 parts SiO_2. The charge given above figures to the ratio of 39.6 parts of total carbon for each 60.4 parts SiO_2, or an excess of 10 percent carbon above the theoretical.

We were led to the use of this charge by a series of runs made in the preliminary work. We were using a small cubical furnace, a foot on a side, inside dimensions, with a granular carbon core 6″ long and $1^3/_{16}$″ diameter. At that time we were limited to the low power supply on which about 100 volts could be obtained across the electrodes at the start. Using only the theoretical amount of carbon, ground to 14 mesh, it was found that the runs went smoothly up to a certain point, usually about 20 minutes after starting, when the power used was about 4 kw. The voltage, which up to this point had been falling gradually, would suddenly rise, and the current would fall almost to zero. As we could not increase the voltage enough to force more current through the resistor, the run had to stop. On dismantling the furnaces, siloxicon was found, but no carborundum whatever except in the core itself. The carbon grains of the core, however, were covered with a yellowish green crystalline coating whose hardness and microscopic appearance showed it to be carborundum. Compare FitzGerald.[4] We had practically formed "Silundum" in the core, the electrical resistance of which was so high that the current could no longer flow. Had we been able to raise the voltage sufficiently to force enough current

through to give a high enough temperature to decompose this SiC into Si and graphite, the run would have gone on, but at the expense of more power.

We explained this formation of SiC in the core on the hypothesis that the first reaction in the charge was $SiO_2 + 2C = 2CO + Si$, the second, $xSiO_2 + uSi + vC = wCO + Si_xC_yO_z$, where $Si_xC_yO_z$ represents the oxycarbides known as siloxicon. The next reaction is either the decomposition of the siloxicon into SiC and CO, or else $Si_xC_yO_z + mC = xSiC + nCO$. The silicon from the first reaction in the outer reacting zone of the furnace passes in past the siloxicon in the next zone nearer the core, and since the carbon particles have become coated with a siloxicon coating through which the silicon vapor will not penetrate easily and since the Si necessary for the second reaction has already reached that point and been absorbed, there is nothing to stay the progress of the silicon vapor until it reaches the core itself. There it finds carbon at a temperature suitable for the direct reaction, $Si + C = SiC$, and hence we form carborundum in our core.

A series of runs was made to test this point. Runs 27, 28 and 29 were made with the theoretical amount of 14-mesh carbon only, and the silundizing of the core occurred in just 20 minutes, in all three. Run 30 had a thin layer of sand right around the core, and the theoretical charge outside this. This should hasten the first reaction and provide free silicon vapor right at the core for the direct formation of SiC. In this run the voltage fell for three minutes and then rose. In 10 minutes the current had dropped to zero. The sand was found to be fused, blackened, and the core silundized. In run 31 we used a charge with almost twice the theoretical amount of carbon. This run went on without a hitch and was continued for $1^1/_4$ hours; 210 grams of SiC contaminated with carbon was obtained, for an expenditure of 8 kwh. The core was perfectly clean at the end of the run.

Then runs with 20 percent and 10 percent excess carbon were tried, running $1^1/_4$ hours, using respectively 9 and 8.3

kwh. Both went smoothly, the first giving 310 grams SiC and the second 375 grams. The cores were perfectly clean at the end of the run.

This showed conclusively the beneficial effects of an excess of carbon, and also showed that better yields were obtained with the lower amounts of carbon, as long as we had enough present to prevent the formation of SiC within the core.

Now if the carbon be present in such large particles that they do not enter entirely into the reaction, but become covered with a coating of siloxicon too thick for the silicon vapor to penetrate, the silicon will pass through to the core. Hence the necessity for the excess of carbon. The theoretical amount of carbon should suffice if the particles are tiny enough. However, if the particles are too small, they will be blown away from the places where they are needed, by the escaping CO. Thus even a large excess of carbon, in large-sized grains, should not be sufficient to prevent the silundizing of the core. To test this, another run was made with the theoretical amount of carbon only, but ground to 32 mesh, over half of it passing a 40-mesh sieve. This run went on smoothly in the main, but after about 25 minutes the voltage rose to 100, showing that some SiC was forming in the core; the current, however, did not fall off so rapidly as in the runs with the theoretical amount of 14 mesh. Soon the voltage fell again and the current rose, showing that we were reading the decomposition temperature of carborundum within the core. After $1^1/_4$ hours the run was stopped. The core showed a little SiC on the exterior grains at the points nearest the electrodes, and the rest of the granules showed distinct graphitization, which is not the case where the carbon core is simply heated to the temperatures attained under these conditions, but only when some carbide former is present. 300 grams SiC were obtained for 9 kwh showing a lower yield of SiC in grams per kwh than in the runs with 20 percent and 10 percent excess of 14-mesh coke, because of the extra power used up on account of the silundization. This

run was just on the ragged edge between success and failure, and showed that the coke would have to be even finer than 32 or 40 mesh if we are to use only the theoretical amount.

As a further check on the size of the grains of coke, we made a run with 10 percent excess carbon, the coke being ground to 12 to 14 mesh, all passing the 14-mesh being discarded, whereas in the previous run with 10 percent excess we used 14 mesh, a large proportion of which would pass a finer sieve. In this run the voltage rose and the current dropped off to zero in 16 minutes. No SiC was obtained in the charge, and the core was found to be silundized.

Thereafter we always used 10 percent excess of 14-mesh coke, as given in the composition of the "normal" charge, and never had any trouble from formation of SiC in the core.

Stansfield [5, p. 150] says that the charge in the carborundum furnace is practically the theoretical, and the data of Richards[6] for coke with the ordinary carbon content, are slightly below the theoretical. However, Mr. Tone, of the Carborundum Co., told the writer that they now use a slight excess of carbon. Some of the Niagara charge was secured and an analysis made, which shows a proportion of 38.9 parts C for each 60.4 parts SiO_2—or an excess of 8 percent above the theoretical. The fineness was about the same as our normal charge, *i. e.*, 14 mesh. By sieving out the larger particles of sawdust and then getting an idea of the relations of sawdust to coke by determinations of the total carbon, volatile and loss on ignition, it was found that the proportion of sawdust in our charge was about the same as that used at Niagara. Hence the composition of our charge is fully justified.

Since this work was done and the above written, Tone[7] has stated that the charge used at Niagara is 35.1 coke, 54.4 sand, 7 sawdust and 3.5 salt, which is an excess of carbon. This figures, taking the same values for carbon content of coke and sawdust as in our materials, to 40.2 parts C per 60.4 parts SiO_2, against the 39.6 parts we have used, a close agreement.

In order to study the reactions in, and the behavior of, the carborundum furnace, it is necessary to have some means of determining the temperature at different points in the furnace, since the reactions that take place, and the range through which they will occur, are functions of the temperature attained, and of the form of the temperature gradient throughout the furnace.

The temperatures reached are far above the range of any known thermocouple; hence we are limited to the use of optical or radiation pyrometers, or to indirect methods. FitzGerald[8] has used the change in density of carbon to show the temperature to which it has been raised. This can, however, only give an approximation to the true value, inasmuch as it can only show the maximum temperature reached. Since there may be, indeed must be, a time factor involved in the transformation of ordinary carbon to denser forms, it will not show temporary fluctuations. Moreover, it does not give the results till the run is over, and it must be based at some time or other on actual temperature measurements, which brings us back to the original problem.

Confining ourselves, then, to optical and radiation instruments, we need, in order to use these instruments, some substance which will be raised to the temperature of the furnace at the point where we wish to measure that temperature, and a method of sighting on this substance. This means a plug of some refractory material at the end of a tube.

Since we are above the melting points of such refractories as alumina or magnesia, we are practically confined to three materials, carbon, graphite and carborundum itself. The choice of these is determined by their refractory qualities, their heat conductivity, and their porosity or permeability to gases and furnace fumes.

The question of fumes is a vital one, since in the carborundum furnace, as in most resistance furnaces, even if made up with only a charge of coke or crushed carbon, fumes are evolved, which, if not removed, obscure the pyrometer readings to such an extent that no results at all can be obtained.

Burgess[9] says that the fume problem is one of the most embarrassing phenomena we have to deal with in optical pyrometery. Potter and Tucker[10] have used a current of hydrogen or other inert gas to sweep out the fumes. In the tubes used in our work we have used air, for practical reasons, inasmuch as the fumes formed as readily in an atmosphere of nitrogen as in air or oxygen, and the troubles from oxidation were not very great, particularly when using carborundum tubes.

Two forms of tubes have been used in this work, first one of carbon, graphite or carborundum, 1½" O.D., 1" I.D., and 12"to 18" long, according to the size of the furnace, bearing a tightly fitted graphite plug at one end. Near the closed end a hole was bored to take a carbon tube ½" O.D., ¼" I.D., and about 12" long, fitted in at right angles, thus making an elbow tube. A glass tube was then fitted into the small carbon tube and all joints between tubes, or plug and tube, luted with a paste made of fine carborundum powder (3 F), waterglass and water, using as little waterglass as was consistent with getting an adherent paste. This paste was also of great value in minimizing oxidation and disintegration of the surface of tubes and electrodes.

Gentle suction from a Chapman pump was then applied through a rubber tube slipped over the glass tube, thus sweeping out the fumes. Attempts to blow out the fumes by a blast of air, hydrogen or nitrogen instead of pulling them out by suction, showed that suction was by far the more efficient, and that it should be applied as near the hot end as possible.

This form of tube was quite efficient up to 1800° C, but it had several disadvantages. It is hard to make a mechanical joint that will withstand 2000° C without leaking. Moreover, the fumes condense in the cooler parts of the small tube, and if not removed, will choke it up entirely.

After an hour or so frequent poking was necessary to keep the small tube open, and this poking often broke the

tube or joint. Hence a second tube was devised, consisting of two tubes, one inside the other, as shown in Fig. 2.

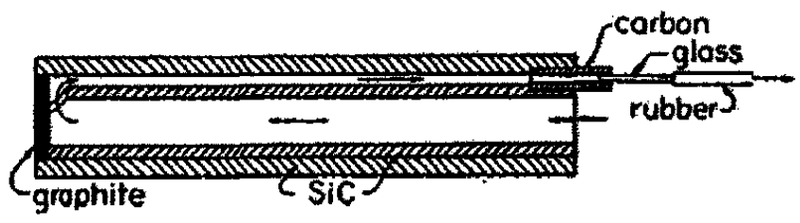

Fig. 2.—Temperature Tube.

The outer tube was $2^1/_2''$ O.D., $1^3/_4''$ I.D., and 12″ to 18″ long and was closed at one end by a very carefully ground and fitted graphite plug $^3/_{16}''$ thick. The inner tube was $1^1/_2''$ O.D., 1″ I.D., and 12″ to 18″ long, and was placed close up against the plug, a notch being cut in the inner end to allow the air to pass freely. A carbon tube $^1/_2''$ O. D., $^1/_4''$ I.D., and 3″ to 4″ long was inserted between the two tubes, cutting them out enough to admit it. A glass tube was then fitted into the small carbon tube and joined by a rubber tube to the suction pump. The joint between the outer and inner tubes was packed with fibrous asbestos and the whole made air-tight by painting with the carborundum-waterglass paste. This tube was highly satisfactory, as by its use the fume difficulties at the temperatures reached were reduced from the most troublesome factor to the least troublesome.

This tube, if properly made, will go up to 2300° without fumes, by the aid of gentle suction. Above that, or in that neighborhood, with very rapid heating, even this tube will show some fume part of the time. Directing a blast of air into the open mouth of the tube will help considerably. For temperatures above 2300° it is best to make the glass tube longer than shown in the figure, so as to prevent melting the rubber tube.

The oxidation of the graphite plug in the current of air is very much less than one would expect. In runs of 4 to 6 hours, where 2500° or 2600° was reached, and the temperature was above 2300° for a considerable part of the time, it was rare that a plug burned through. By making the plug

thicker, or by only using the suction during intermittent temperature readings, its life may be prolonged still further.

One difficulty still remains. At temperatures from well below 2000° up, crystals of SiC form inside the tube, and unless constantly poked out with a stout carbon or graphite rod, will gradually contract the bore of the inner tube near the plug. This must be especially watched in using a radiation pyrometer where the angular opening is such as to require the full field of the plug.

This formation of SiC crystals is interesting, since it must come either from direct sublimation of SiC, by the combination of Si vapor with the carbon in the walls of the tube, or by the direct union of Si vapor with the carbon vapor from the decomposition of SiC. Since the crystals formed in as great abundance in tubes made of carborundum, without much free carbon, we incline to the last view.

In connection with this it is worthy of note that the almost black carborundum usually obtained is only colored in that way when at some hotter portion of the furnace we have reached the decomposition point of SiC into graphite. In several runs made in the preliminary part of this work where the power available was low, we made carborundum without reaching its decomposition temperature at any point, as shown by the absence of graphite. In every such case the carborundum was of a greenish golden color. We understand that at Niagara whenever they find a portion of the carborundum free from this black color, on tearing down the furnace, these lighter colored crystals are separated and kept for special work, such as making dentist's wheels. If they would be content with a smaller yield of carborundum, this light colored product could be obtained at will by regulating the temperature so as not to exceed the decomposition point. Moissan [11, p. 353] has made practically pure SiC, which is colorless. Acheson[12] says the black color is due to opaque crystals of free graphitic carbon.

Let us come back to the question of fumes for a moment, and consider their probable composition. They might con-

sist of Si and C vapor, of minute particles of charge carried off by the CO, of NaCl vapor, or of the vapor of compounds present in the ash of the coke, or formed from this ash, or of disintegrated particles from the tube itself. The last cause is certainly present, as there is always some disintegration of the walls of the tube, which is especially noticeable both on the outside and inside, where the tube goes through the firebrick walls, just at the junction of charge and outside air. The electrodes also disintegrate at this point, the CO from the furnace burning to CO_2, which again reduces to CO in contact with the hot carbon.

However, the portion of the fumes which condenses in the space between the outer and inner tubes, and in the glass and rubber tubes, is a white powder which collects into a mossy sort of structure. Analysis of this shows it to be very slightly attacked by acids other than HF, and to contain almost nothing but SiO_2 and CaO. In one of the first preliminary runs a carbon tube was placed transversely through the furnace and became filled with fumes. It was closed by carbon plugs at each end and allowed to cool undisturbed. Quite a few needle-like crystals were found in the tube, some of them being 1.5 cm long. They were apparently hexagonal and showed peculiar etching figures when treated with HF. Microchemical analysis showed them to contain SiO_2 and CaO with traces of Na, Fe, and Mg. They may perhaps be calcium metasilicate, $CaSiO_3$, as described by Allen, White and Wright[13].

The material for the temperature tubes may be graphite, carbon, or a carborundum composition. The last is the most satisfactory for use in the carborundum furnace. We were led to the use of this material by the desire to have a substance which, when heated, would have as nearly as possible the same temperature gradient as that of the charge. Since in the zone nearest the core we have the carborundum decomposing to graphite, the only way to get a tube which would consist of graphite in the graphite zone and carborundum in the carborundum zone, and to have the graphite zone

in the tube follow that in the charge as it increased, was to start with carborundum, which would automatically decompose, just as the charge does. How nearly the temperature gradients really agree will be discussed later.

With this idea in view, we requested the National Carbon Co. to make up for us tubes containing as much carborundum as possible. They took up the problem, and furnished us with tubes of various sizes which proved to be very satisfactory. Though these tubes were made at our suggestion and on our order, the makers refused to tell us their composition. Analysis shows, however, that the finished tubes contain from 70 percent to 80 percent of fairly finely ground SiC, the remainder being mainly carbon, either put in as such or derived from the binder.

A few rough determinations of some of the physical properties of the carborundum tubes were made. They are naturally very hard to work and destructive to tools. They can be sawed, with the use of some elbow grease, it is true, with a saw practically devoid of teeth, the particles of SiC torn torn off acting as the abrasive, and giving us a sort of band saw. A rapidly rotating carborundum wheel was of great value in working the tubes.

A rough determination of the apparent density (not the true density for the air-free material) gave 2.22 for the SiC tube, against 1.53 for the ordinary carbon tube.

Some crushing and transverse tests were made to compare them with carbon tubes, which are tabulated in Table I. The testing machine was a 50,000-lb. Riehlé belonging to the Sibley College of Mechanical Engineering of Cornell University:

TABLE I

Crushing Strength

Material	Average O.D. inches	Average I.D. inches	Average height inches	Broke at pounds	Strength lbs. per sq. in.
Carbon	1.52	1.00	0.49	7200	6700
"	1.56	1.00	1.48	5100	4225
"	1.56	1.01	1.49	6100	5490[1]
"	1.53	0.99	1.54	6800	6360
				Aver.,	5770
Carborundum	1.50	0.89	1.53	5400	4720
"	1.54	0.88	1.52	5050	4020
"	1.53	0.90	1.53	6700	5520
				Aver.,	4770

$$\text{Formula } S = \frac{P}{\pi/4\,(d_1^2 - d_2^2)}.$$

Transverse Strength

Material	Average O.D. inches	Average I.D. inches	Test length inches	Broke at pounds	Strength lbs. per sq. in.
Carbon	1.56	1.02	16.0	160	2890
Carborundum	1.52	0.88	16.0	280	2910
"	1.52	0.89	16.0	220	2100

$$\text{Formula } S = \frac{Plr_1}{\pi(r_1^4 - r_2^4)}.$$

Only one transverse test was made on carbon, as at that time there was only the one tube of the required length in stock. The carborundum shows up slightly less well in these tests, but the strength of both materials is of the same order of magnitude.

A test was then made to determine the relative permeability of the two tubes to gases at room temperature. The tubes were closed at one end by a solid rubber stopper and at

[1] Cracked lengthwise at 2000 lbs.

the other with a rubber stopper bearing a glass tube which was connected through a manometer to a motor-driven Geryk oil pump. All joints and connections were carefully shellaced. The dimensions of the tubes are given in Table II:

TABLE II

Material	Average O.D. inches	Average I.D. inches	Average thickness of wall inches	Height of unshellaced portion	Vacuum obtained cm Hg.
Carbon	1.55	1.02	0.53	5.30	19.0
Carborundum	1.52	0.895	0.625	6.25	8.5

After an hour's pumping the carbon tube showed a vacuum of 19 cm of mercury, or $^1/_4$ atm.; further pumping did not increase the vacuum. Under similar conditions the carborundum tube showed 8.5 cm, or $^1/_8$ atm.

On cutting off the pump, neither tube would maintain the vacuum even momentarily, though the leakage back through the carborundum tube was the slower. This easily explains why the fumes pass from the furnace into the tubes, and shows that, though both are very permeable, the carborundum is the less so.

In resistance to oxidation and durability the carborundum tubes were distinctly superior to the carbon tubes. Of course a tube which has been raised to graphitization temperatures cannot be used again, since the temperature gradient through it the second time will not be the same as that of the furnace till the furnace has reached the same condition in the second run that it was in at the end of the first. However, by making the tubes longer than is necessary at first, the graphitized portion can be cut off and the shortened tube used again. The second shipment of carborundum tubes was not quite as dense as the first, and they were not so desirable, though their dimensions were more accurate than those ordered than the first lot, which were about 0.9″ I.D. instead of 1.0″. Even these, however, were vastly superior to the carbon tubes.

In using this form of tube in the actual measurement of furnace temperatures, we have several factors to consider. We have (1) the temperature gradient through the tube and its relation to that through the charge, (2) the uniformity of heating of the plug, (3) the difference in temperature between the outer and inner surfaces of the plug, (4) the effect of the current of air through the tube, and (5) the deviation from "black body radiation" of the plug. Let us take these up in order.

To measure the temperature of any part of the furnace by our tube, we must be certain that the difference in temperature gradient between the furnace is small, in order that too high or too low heat conduction through the tube may not cause the heat to be drained away from, or piled up at, the plug. If we cannot attain this exactly, we must come as near to it as possible. This is important when we are using simply the plug in the end of the tube, but when we use a movable plug to measure the temperature at different points through the tube, it is of prime importance. From a theoretical point of view, the carborundum tubes should be the best in this respect.

To test this out, a run was made on three tubes, a carbon, a graphite and a carborundum. A furnace was built of the dimensions given in Fig. I, and filled with 150 lbs. of the normal charge. The tubes were all of the dimensions given for Fig. 2, and 12″ long, and were like that figure save that the glass tube was luted directly into the space between the two tubes, no small carbon tube being used. The plugs were placed against the core, which was 4″ high, thus extending $^3/_4$″ above and below the plug. The core was built with great care as to uniformity of cross section, by carefully leveling the charge to the level of the bottom of the electrodes, placing parallel sheet iron strips across past each side of the electrodes, filling in to the top of the strips with charge, then filling the trough thus made with the granular carbon core and leveling the top, removing the iron strips, and filling in the rest of the charge. The tubes extended through the

wall about 1″ into the open air. They were spaced equally along the 16″ core, *i. e.*, with their middle points 4″ from the middle point of the adjacent tubes, or from the junction of core and electrode. Previous runs had shown that the cooling effect of the electrodes did not extend 4″ into the core. The graphite tube (B, Table III) was placed in the middle, the carbon (A) on one side and the carborundum (C) on the other.

Midway between the graphite and carborundum tubes, and exactly 3″ from the nearer surface of the plug ($3^{9}/_{16}$″ from the core) was placed the junction of a Pt, Pt 10 percent Rh thermocouple, in a porcelain protection tube, the end of which has been ground off to a thickness of 0.4 mm, to avoid as much as possible the heating lag of the couple due to the porcelain wall. Graphite plugs, $^{8}/_{16}$″ thick, and of such size as to slip easily in the tubes, were mounted on small graphite rods, and the rods graduated to read the distance of the nearer surface of the movable plug from the nearer surface of the stationary plug at the end of the tube. By setting these movable plugs 3″ from the stationary ones and sighting on them with the Wanner pyrometer, we get a means of reading the temperature at that point in each tube, which may be compared with the temperature shown by the thermocouple at the same distance from the core, which may be taken as the true temperature of the furnace at that point. The thermocouple had been checked against one certified by the Bureau of Standards, read on a potentiometer, and the Wanner pyrometer had been checked against this thermocouple by means of an experimental "black body" in a platinum furnace as well as checked by a spectrophotometer on the basis of Wien's law, as will be explained later.

By adjustment of transformer switches and the field rheostat of the generator, the power was varied so as to control the temperature as desired.

Tables III, IV, and V give the log of this run. The data of Table V are plotted in Fig. 11.

TABLE III
Run of Jan. 25, 1909

Time	Volts	Amps.	K. W.	Temperature—stationary plug by Wanner			Temperature movable plugs 3″ from stationary plugs by Wanner			Charge temp. 3″ from stationary plugs by thermo couple
				A carbon	B graphite	C SiC	A carbon	B graphite	C SiC	
7:37	150	—	—	—	—	—	—	—	—	20°
7:52	140	25	3.5	1050°	985°	1060°	—	—	—	70
7:56	—	—	—	1100	1040[1]	1140	—	—	—	90
8:00	135	50	6.7	1310	1240	1330	—	—	—	100[2]
8:18	104	150	15.6	—	—	—	1030°	1055°	below 900	485[2]
8:22	104	150	15.6	—	—	—	1040	1135	1014	780[2]
8:25	86	150	12.9	1785	1785	1785	1110	1175	1055	950[2]
8:30	94	110	10.3	1770	1770	1770	1110	1190	1110	1110
8:36	—	—	—	1755	1740	1755	1175	1245	1160	1170
8:45	100	230	23.0	—	—	—	—	—	—	—
8:50	82	170	14.0	2005	2005	2005	1415	1440	1370	1380
8:55	—	—	—	—	—	—	1430	1455	1380	1390
9:00	95	170	16.1	1960	1930	1945	1455	1470[3]	1415	1420
9:05	88	180	15.8	—	—	—	1470	1490	1440	1450
9:15	—	—	—	—	—	—	1525	1550	1480	1485
9:20	80	200	16.0	—	—	—	1550	1570	1505	1495[5]
9:30	77	200	15.4	—[4]	—	—	—	—	—	—

[1] The projecting end of the graphite tube hisses when water is dropped on it. The others do not at this time.

[2] Thermocouple lag affects these readings. The thermocouple readings were increasing at a much more rapid rate than those of the optical pyrometer on the movable plugs.

[3] The graphite tube was red hot outside the furnace at this time, the others were not. It was possible to bear the hand on the top of the furnace charge at this time.

[4] The carbon tube was disintegrating to powder inside and fuming. No more readings were taken with it.

[5] The thermocouple and protection tube were taken out at this point in the run. Readings were then taken with the movable plugs to show the gradients through the graphite and SiC tubes.

TABLE IV

Time	Volts	Amps.	K. W.	Temp. graphite tube (B) stationary plug	Temp. graphite tube (B) 3″ back	Temp. SiC tube (C) stationary plug	Temp. SiC tube (C) 3″ back
9:35	..	...	....	2000	1580	2000	1515
9:50	80	170	13.6	....	....	....	...
9:52	100	200	20.0	....	....	....	....
9:55	80	225	18.0	....	....	2080	....
10:00	90	300	27.0	....	....	2120	....
10:03	83	320	26.6	....	....	2160	....
10:07	72	310	22.3	[1]	....	2200	....
10:15	67	300	20.1	....	....	2220	1660
10:20	70	290	20.3	....	....	2220	....
10:25	71	290	20 6	....	....	2220	....
10:30	69	290	20.0	[2]	....	2220	....

TABLE V

Time	Temps. in graphite tube (B)				Temps. in SiC tube (C)						
	At plug	1″ back	2″ back	3″ back	At plug	½″ back	1″ back	1½″ back	2″ back	2½″ back	3″ back
9:35	2000	1885	1730	1580	2000	....	1860	....	1670	....	1515
10:07	....	....	....	...	2220	2100	2005	1930	1830	1755	1660

There was graphite on the end of the SiC tube at the end of the run. This showed that we were slightly above the decomposition temperature. The highest temperature reached was 2220°, plus the correction for drop through the plug, to be determined later. The carbon tube was badly corroded at the end of the run, the graphite somewhat less so, while the carborundum tube was but slightly attacked, being in very good shape at the end of the run. The glass tube extending into the graphite tube had fused together, those in the other two tubes had not softened.

[1] The rubber tube on the graphite tube was melting. The glass tube was softening. No more readings taken in this tube.

[2] At the end of the run the part of the graphite tube extending outside the furnace was at 935° when sighted on with the Wanner. The SiC tube had not begun to glow outside the furnace.

Table VI shows the deviations of the temperatures in the three tubes at the three-inch point from that of the thermocouple, after the thermocouple lag due to rapid heating had been overcome:

TABLE VI

Temp. by thermocouple	Deviations in degrees C		
	Carbon	Graphite	SiC
1110	0	+80	0
1170	+ 5	+75	—10
1380	+35	+60	—10
1390	+40	+65	—10
1420	+35	+50	— 5
1450	+20	+40	—10
1485	+40	+65	— 5
1495	+55	+75	+10
Average deviation	+30	+65	— 5

At this particular rate of heating there is no noticeable error in the readings of the carbon tube up to 1200°, but thereafter the error becomes serious. The agreement in the case of the SiC tube is uniformly good, holding for a range of 400° and for 50 minutes. It is plain that the graphite tube gives much too flat a gradient, compared with that through the furnace, and temperatures measured in that tube by the movable plug give readings above the true furnace temperature. This is shown not only by the data, but also from the foot-notes, as the outer end of the graphite tube was at all times much hotter than the outside of the charge. The carbon tube was better, but even that gives too high readings, while the caborundum tube gives correct readings within the limits of error in setting the Wanner pyrometer.

The second point, the uniformity of heating of the plug over the field of view, varying from $^7/_8$″ to 1″ diameter in the tubes used, may be dismissed with a few words. If we use a very small core and place the tube so that, say, only the lower part of the plug touches the core, that part would begin

to glow first, but even in such extreme cases the field becomes practically uniform above 1200° when explored by the Wanner or Morse pyrometers. Using a core large enough to give a uniform source of heat as large as, or larger, than the plug, no trouble from this source was noted at any temperature.

The third point, the difference in temperature between the outer and inner surfaces of the plug, requires a little more attention, since what we wish to measure is the temperature clear at the end of the plug, and what is read is the temperature at the nearer surface. Measurements were made to determine this factor, using $^1/_8''$ graphite plugs in SiC tubes. The charge was of the normal composition. The method used was to insert a second tube in the furnace, the reading on the plug in which will show if we are holding the temperature constant, then with the temperature remaining constant, to insert, one at a time, $^1/_8''$ plugs ground with true surfaces, so that four plugs would stack up the just $^1/_2''$, and read the temperatures of their exposed surfaces by the Wanner.

It was found by inserting a solid plug $^1/_2''$ thick that the contacts were so good that, within the limits in reading, the solid plug gave the same results as four $^1/_8''$ plugs. The plugs were jammed in tightly and held in place by a small graphite rod. The results follow:

TABLE VII

Temp. visible surface original plug	Temp. visible surface added plug $^1/_8''$ back	$^1/_4''$ back	Correction for $^3/_{16}''$ plug
1350°	1326°	1305°	+35°
1550	1524	1508	+31
1665	1645	1615	+30
1730	1712	1694	+27
2050	2035	2020	+22
2150	2136	2121	+20
2160	2149	2136	+17

From 1800° up to 2500° a correction of +20° added to the temperature read on the visible surface, will give values close enough to the true temperature at the back of the plug.

These readings were taken with the furnace at a constant temperature; *i. e.*, practically at a stationary state. With very rapid rates of heating the drop will be somewhat greater. With large furnaces, and hence a flatter gradient, it will be rather less. However, the chief use we had made of this correction is in determining the temperature of formation and decomposition of SiC. These were determined in furnaces of the same size as the one used in this determination, and with the furnace at almost a stationary state, so the conditions are quite comparable.

Now we come to the effect of the current of air. Although we only use as gentle suction as will avail to carry off the fumes, it is obvious that there must be some cooling effect due to it. Whether it will be of such magnitude as to affect the readings appreciably, is another question. This was tested at several temperatures, sometimes in the regular furnace when conditions were favorable, as in cooling down from higher temperatures, when the suction could occasionally be left off for a few minutes without the formation of fumes; and sometimes in special furnaces packed with crushed SiC, which evolves less fume than the normal charge. For instance, at 960° and at 1190° in the later form of the tube and at 1740° in the elbow form, no change that could be detected by the optical pyrometer was noted whether the suction was on or off. In the run at 1190° a thermocouple in a porcelain tube was inserted into the tube against the plug to aid in holding the furnace at a constant temperature. The thermocouple readings are lower than the plug temperatures owing to the temperature drop through the 2 mm of porcelain between plug and couple. Readings were taken at 3-minute intervals:

TABLE VIII

Rising Temperatures

Temp. by thermocouple	Temp. by Wanner	Suction
1147	1184	off
1149	1187	on
1153	1189	off

Falling Temperature

1153	1187	off
1152	1184	off
1148	1181	on
1146	1177	off
1145	1174	off

In the later type of tube we once got conditions so that no fumes were evolved for a few minutes at 2000°. No difference could be detected whether the suction was on or off. Again, at 2200°, the fumes were once slight and when the suction was off lay quietly in the lower part of the tube. Sighting on the upper part of the plug, and turning the suction on full, no change in temperature could be observed. In the double tube a good deal of the cooling effect of the incoming air, which cools the inner tube and is itself heated before passing by the plug, must be counteracted by the air that has passed the plug, cooling off on its outward passage and giving up its heat to the outside of the inner tube, which thus is heated almost enough to compensate for the heating it itself exerts on the incoming air. The air heated by passing through a foot or more of tube at a slow rate would not be expected to cool the plug very much, and though in theory there must be some cooling, it is not detectable by optical pyrometers, and hence is negligible. At any rate, we cannot get on without the current of air.

We now come to the last point, the deviation of the radiation of the plug from true "black body" radiation.

All bodies heated to the same actual temperature do not emit the same amount of radiation. For instance, if we

look at a glowing carbon strip and a smooth platinum strip, both heated to the same temperature, the carbon appears to be much the hotter. If we sight an optical or radiation pyrometer on the surface of a bath of molten copper, the temperature read will be much lower than the true temperature of the bath[14]. This is due to the fact that the copper and platinum both have high reflecting power, and consequently low emissive power, since for an opaque body the sum of the reflecting and emissive powers is unity[15]. In 1860 Kirchhoff[16] brought out the idea of a theoretical "black body," which is one with perfect emissive power and zero reflecting power. Synonymous with this, and better and more expressive, though less used, is the term "complete radiator" [17, 18].

If a substance, say platinum, that does not give complete radiation is made into a hollow sphere, this sphere uniformly heated and the radiation observed through a small opening, this radiation will be exactly the same as that of a true black body, no matter how far the surface radiation may be from complete, because the radiation reflected back by any portion of the surface is just great enough to make up for the amount that is not radiated directly from that portion of the surface, because of its lack of perfect surface radiation. In other words, a hot body in the open air rarely approximates complete radiation, since almost everything reflects some radiation, and does not absorb all that falls upon it. Only a body that would absorb 100 percent of the radiation falling on it will emit 100 percent of the radiation that it is entitled to, barring reflecting power, at that temperature. On the other hand, in a uniformly heated enclosure, it is quite an indifferent matter what the hot body is composed of, or what its surface is.

However, if we have a reflecting material, *i. e.*, not a complete radiator, in an enclosure, as a sphere or tube, which is not uniformly heated, then in this case the reflection does not make up for the lack of complete radiation, for the radiation that is reflected by the surface under consideration

comes from a region of higher or lower temperature than this surface. This is not negligible, since the intensity of the red rays emitted by a body at 1300° C is about 130 times, and at 2000° C more than 2100 times as great as at 1000° C [18, p. 49].

Hence in determining the "blackness" of any body we have two distinct factors to consider; first the approach to complete surface radiation, which means an approach to zero reflecting power, and second, the approach to a condition of uniform heating throughout the enclosure containing the body. If either factor is 100 percent, if either the surface radiation is complete, or if the enclosure temperature is exactly uniform, changes in the other factor will have no effect.

Most fortunately, lampblack or matt-surfaced carbon or graphite, gives, even in the open, the nearest approach to complete, or black body surface radiation, of any substance known [18, p. 50] [19, p. 177] [20]. Hence we have only a few percents or probably a few tenths of a percent of deviation from complete radiation to make up by having a uniformly heated enclosure in our temperature tube. Moreover, carbon does not show selective radiation or absorption [20, p. 327] [21], hence as good an approach to black body radiation shown for a single wave-length, say in the red, as used in the optical pyrometers, should hold for the total radiation, visible and invisible, as used in the radiation pyrometers.

We have stated above that carbon approaches complete radiation; the next question is, is this true not only for low red heats, but also for the highest temperatures? Will it become more of a reflector, and a poorer black body with rising temperature? The radiation emitted of course increases with the temperature, but our problem is, will the ratio of the emissive and reflecting power vary with changes of temperature? No measurements of this appear to have been made on carbon, but for platinum, where we would expect a change, if any occurs in any material, data are available. Waidner and Burgess, in a paper [22, p. 347] published in March, 1905, plot the deviation from black body radiation of platinum against the true temperatures as a straight line.

Now it is stated earlier in this same paper, that Wien's law holds for bodies which deviate from black body radiation, but with different values of the constants. We shall deal with this law a little later, but we will anticipate for a moment. In this paper by Waidner and Burgess, it is shown that the Wien law may be expressed as follows: $\log I = K_1 + K_2 \frac{1}{T}$, where I is the intensity of light of a definite wave length, T the absolute temperature, and K_1, K_2 constants. Then for the same intensity we may express it

$$\log I = C_1 + C_2 \frac{1}{B}$$

where B is the "black body" temperature of a body not a complete radiator, and C_1, C_2, the corresponding constants. B is the absolute temperature to which a true black body would have to be raised to give equal photometric brightness. B is always less than T and C_1 and C_2 always less than K_1 and K_2.

Equating the values for the same intensity, we get

$$K_1 + K_2 \frac{1}{T} = C_1 + C_2 \frac{1}{B}, \text{ or } \frac{1}{T} = \frac{C_1 - K_1}{K_2} + \frac{C_2}{K_2} \frac{1}{B},$$

or a linear relation between $\frac{1}{T}$ and $\frac{1}{B}$. If this relation, which follows from Waidner and Burgess's own statements, be true, then it is an algebraic impossibility to have a linear relation between T — B and T, which is what they are plotting in their curve. This impossibility might be straightened out if we assume that the constants K_1, K_2, C_1, C_2, are not absolutely constant. This will be referred to later. But Waidner and Burgess do not dodge the question in this way, for when Lucas[23] showed that there is a linear relation between $\frac{1}{T}$ and $\frac{1}{B}$, they accepted his results[24] and backed them up by data of their own. Still later [25, p. 178] they give a curve for the radiation from platinum showing a curved line relation between T — B and T, which when transformed

into the values of $\frac{1}{T}$ and $\frac{1}{B}$ shows a straight line relation between these two quantities. They do not, however, comment on or explain the reason for the discrepancy between this curve and their earlier curve, evidently thinking that their acceptance of Lucas's results had tacitly corrected their first erroneous curve. The two different forms of the same curve published by the same people without any explanation puzzled us for some time, however.

Lucas's results, and the later ones of Waidner and Burgess, then, show that polished platinum is just so far and no farther from a complete radiator at one temperature as at another, and while the results of Lummer, and Pringsheim [26] [27], which will be referred to later, throw a shadow of doubt on this, we may say at least that even for platinum, with its great deviation from the condition of a complete radiator, there is no definite proof of any appreciable change in "blackness" for wave-lengths in the visible spectrum. For other wave lengths, see Coblentz[28]. Hence for carbon, which deviates so little anyway, we are pretty safe in assuming no great increase in this deviation. Waidner and Burgess point out [24. p. 445] that this constant deviation need only hold in case the substance undergoes no chemical change during the range of temperature used. It will probably be safer to except also changes of state, such as metal passing through an inversion point, or from the solid to the liquid state [22. p. 240, 248] [24. p. 445] [29. p. 14]. On the other hand, see curve, Waidner and Burgess [25. p. 186].

Since our graphite plug, if graphitized at a high enough temperature, will not change through our temperature range, this need not worry us. Thus we know that the emissive power of our plug will not grow worse with rising temperatures; on the other hand, the fraction of a percent it lacks of complete surface radiation will be more and more made up as our tube becomes more uniformly heated through the flattening of the temperature gradient right at the plug with higher temperatures.

Hence we expect that the deviation of our tube from true black body radiation will be very small at the worst.

One precaution is necessary; *polished* graphite has considerable reflecting power. In an unpublished observation by Mr. V. Skillman, of this laboratory, a layer of graphite powder was placed over half of the bottom of a very smooth, polished graphite crucible and the whole heated to about 1750° in an Arsem vacuum furnace. The polished graphite read much lower than the powder, when sighted on with the Wanner pyrometer, although Arsem[30] states that all bodies heated in the vacuum furnace show black body radiation. Hence care was taken to make all plugs with a distinctly matt surface. Oxidation of the surface of the plug during use will tend to increase the "blackness" through pittting [35, p. 40]. When we deal with total radiation instead of monochromatic radiation, the "blackness" of bodies that are not complete radiators increases with the temperature [22, p. 199], hence we are running under still more favorable conditions in this case, with rising temperature.

The uniformity of heating may be tested qualitatively up to 1750° C by holding a piece of smooth platinum against the plug at the end of the tube. If the tube is uniformly heated, the platinum will give off black body radiation, and be invisible against the carbon. The degree of visibility will show something of the error present through lack of uniform heating, *i. e.*, it will tend to show how much of those few tenths of a percent the graphite plug lacks of being a complete radiator, we are making up. At 1100°, in our second form of tube, the platinum is quite visible, but at 1500° one has to know just where it is to find it against the plug, and above 1600° it is lost entirely. Lampen[31] has attempted to determine whether a hot plug showed deviation from a black body, by placing a bare thermocouple near it, or one in a 1 mm thick fireclay protection tube, directly against it, and reading the temperature of the plug by the Wanner pyrometer. This was compared with the thermo-

couple reading, and was always higher, sometimes by 20–25° C.

Now unless the thermocouple is actually in contact with the plug, it will read low (see Table VIII, where we have a difference of 40° for 2 mm of porcelain). Now if the plug shows deviation from black body radiation, it will also read lower than the true temperature, since no body at the same photometric brightness as the black body can have a higher temperature. Hence, if both the methods of reading may give us low results, an approximate agreement between them tells us little or nothing as to the true temperature of the plug.

However, we can really test the "total blackness" of our plug, that is, the effect of both the factors that affect it, combined, by the application of Wien's law, and to this we will now turn our attention.

In 1896 Wien[32] took up the problem of the distribution of energy in the spectrum of a black body. He found that the energy for a given wave length was expressed by

$$I = c_1 \lambda^{-n} e^{-c_2/\lambda T},$$

where I is the energy, or intensity of light corresponding to wave length λ, T the absolute temperature of the black body, e the base of the Napierian system of logarithms, c_1, c_2 and n constants [19, p. 183] [22, p. 204].

For a black body, n is 5 [27, p. 717]. This formula was checked by several observers and found to hold for the visible spectrum, but deviations were found for longer wave lengths. Planck, however, deduced a similar expression from purely thermodynamic principles. This holds for all wave lengths and is

$$I = c_1 \lambda^{-n} \frac{1}{e^{c_2/\lambda T} - 1}.$$

When this is expanded in a power series, we get an expression the first term of which is the Wien equation given above, and further terms of which are negligible for wave-lengths in the visible spectrum[27]. Waidner says [18, p. 51], "For the

wave-lengths of the visible spectrum, Wien's equation represents the results of experiment with every required degree of precision, since for values of T not exceeding 3000, Wien's and Planck's equations differ by less than 1 percent. The former may, therefore, within the visible spectrum, be used for extrapolation to the highest attainable temperatures (4000° C or more)."

Now consider the Wien equation. Taking the natural logarithm of each side we get

$$\log I = \log c_1 - n \log \lambda - \frac{c_2}{\lambda} \log e \frac{I}{T}.$$

putting

$$\log c_1 - n \log \lambda = K_1 \text{ and } \frac{c_2}{\lambda} \log e = K_2,$$

we get

$$\log I = K_1 - K_2 \frac{I}{T}.$$

Waidner and Burgess [22, p. 210] err in giving this without the minus sign before the second constant, which would show the intensity of the light to decrease with rising temperature, which is absurd.

Now we know that the intensity of light varies as the square of the distance, so if for any two intensities I_o and I_1, at temperatures T_o and T_1, we have the distances x_o and x_1, we get

$$\frac{I_o}{I_1} = \frac{x_o^2}{x_1^2} = \frac{c_1 \lambda^{-n} e^{-c_2/\lambda T_o}}{c_1 \lambda^{-n} e^{-c_2/\lambda T_1}}.$$

Taking logarithms again, we have:

$$\log I_o - \log I_1 = 2 \log x_o - 2 \log x_1 = \frac{c_2}{\lambda} \log e \left(\frac{1}{T_1} - \frac{1}{T_o} \right).$$

Then let

$$\frac{c_2}{2\lambda} \log e = C,$$

and we get

$$\log x_o - \text{ og } x_1 = C \left(\frac{1}{T_1} - \frac{1}{T_o} \right).$$

But if we measure the temperature of the hot body at some

temperature T_1 by any convenient means, we have a measurable x, corresponding to it, and knowing C, the only unknown factors left are x_1 and T_o.

We may write the above as

$$\log x_o = \left(\log x_1 + \frac{C}{T_1}\right) - C\,\frac{1}{T_o}.$$

Here C and the expression in parenthesis are constants, and we may write

$$\log x_o = R - C\,\frac{1}{T},$$

which is a linear relation between $\log x_o$ and $\frac{1}{T_o}$. When we have a means of measuring x_o, we know T_o, and on this is based a method for the calibration of optical pyrometers, of which we shall shortly make use.

Wien's law applies to bodies which are not complete radiators as well as to the black body, c_1, c_2 and n varying with the nature of the substance [22, p. 210]. Since all of these save c_2 cancel out in the equation as we shall apply it, we are concerned only with that, and so will consider its constancy and value.

Lummer and Pringsheim[26] say that c_2 has a progressive variation such that the curves plotted between log I or log x and $\frac{1}{T}$ are convex to the $\frac{1}{T}$ axis. In the data given in the literature we often find that the values for c_2 for what is intended to be a black body, are considerably greater at the lower temperatures than the mean value for all temperatures. It is quite possible, though no one seems to have pointed it out, that this is due to the greater deviation from a condition of uniform heating right around the hot body in the ordinary electrically heated "black body" at the lower temperatures. In this connection, see Day and Sosman [33, p. 102].

At all events, in those experiments in which the workers consider that they attain most nearly to black body conditions, and especially at the higher temperatures, the values for c_2 become more and more constant, and the value usually

taken, $c_2 = 14500$ for a complete radiator, is perhaps the means of all reliable determinations. Nutting[27] gives c_2 as 14500 ± 300, which seems to be about the proper limits to set. Inasmuch, however, as the value for c_2 given by bodies that are not complete radiators is higher than that given by the black body, we incline strongly toward the lower value of c_2 for a complete radiator. Moreover, Holborn and Valentiner[34] in the most recent careful work on the value of c_2, give, as the result of some 140 very careful and closely agreeing determinations, the value 14200 ± 1 percent. Their temperatures to 1600° C were based on the nitrogen thermometer. This leads them to the figure 1789° C for the melting point of platinum. The difference in the values used for c_2 largely accounts for the failure of the figure 1753° obtained by Waidner and Burgess[25] to check with this figure, and Waidner[18] says that on account of the uncertainty in the value of c_2 further work must be done on the determination of this constant. It is to be hoped that Day and Sosman, at the Geophysical laboratory, will take up this problem, since their nitrogen thermometer has undoubtedly been brought to the highest state of perfection yet attained, and an extension of their very careful methods to this question would do much to clear away the uncertainties now attending the measurement of temperatures above 1600° C.

We shall refer again to the value of c_2.

Many references on the subject of black body radiation, Wien's law, and the value of c_2 have been consulted, and will be found in the bibliography[35, 64]. Chwolson, in Vol. 2, Part 1, and Vol. 3, Part 1, of his Traité de Physique, gives a good summary of the whole subject, and a copious bibliography.

Now since C in the equation,

$$\log x_0 = R - C \frac{I}{T_0}$$

depends on c_2 and λ, and gives the slope of the $\log x_0$, $\frac{I}{T_0}$ curve, this slope will give us a means of testing the deviation

from black body radiation of our tube, because for bodies that are not complete radiators, c_2 is greater than 14500, or 14200, whichever is the true value. A slope which figures back to a large value, say 15000, would show considerable deviation, while one close to 14200 would show that we are getting practically black body radiation.

In order to determine this deviation by the application of Wien's law to our problem, we must have some means of measuring the ratio $\frac{I_0}{I_t}$, or $\frac{x_0^2}{x_t^2}$.

The spectrophotometer is such a means.

This instrument[65] in the form used in this work (Fig. 3), consists of two collimator slits, A and B, and two

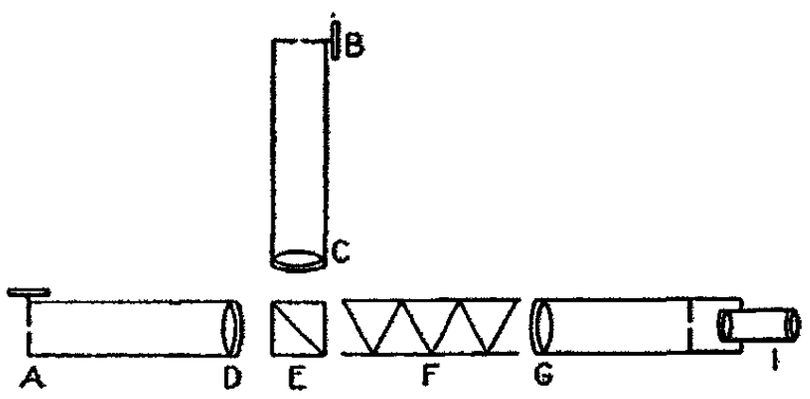

Fig. 3.—Diagram of Spectrophotometer.

lenses, C and D, which transmit light from two sources through a Lummer-Brodhun comparison cube, made of two totally reflecting prisms with such a figure etched or ground upon their faces as to give a quadruple field by which the intensity of the two lights may be matched. Both Fleming [66, p. 757] and Lummer and Brodhun[67] give drawings of the field.

This field is now viewed through a series of direct vision prisms F, and a lens G. A small telescope eyepiece, which may be removed at will, fits in at I, back of a cross-hair. The system of prisms, lens and eyepiece may be swung over a graduated scale, so as to allow setting for any desired wave length, and may be clamped in position. Thus we use practically monochromatic light. If then, we set the instrument to use red light (0.66μ), and place two sources of light of the same intensity before A and B, at equal distances from

the slits, with the slit width of A and B the same, the distance of A and B from E the same, and of the absorption of light through both collimator systems is the same, the fields will be equally illuminated. Or, if one light source is of greater intensity than the other, it may be put at such a distance from its slit that the fields again match. Measuring the distances from light sources to slits gives us x_0 and x_1 for our formula.

The spectrophotometer used in this work was loaned by the Department of Physics, and was the instrument used by Prof. E. L. Nichols in his work on Theories of the Color of the Sky[05], with the single difference that the Nicol prism shown in his diagram was not used.

Theoretically, there are two ways in which the instrument might be used: knowing the temperature of one light source, we may vary its distance from the instrument, and also vary the distance of the other light, or with a source of light that cannot be moved, as a large electric furnace, we may vary the distance from that source, of the whole system, instrument and other light source. Or with a light source of constant intensity at a constant distance from the instrument, we may vary the distance of the whole system from the unknown source. Then knowing the distance and temperature of the source whose temperature is thereafter to be sought, for any one temperature or for any range of temperature, we can figure the value for unknown higher temperatures from the distances corresponding to them.

In a way, the first method would be the easier, since we may bring our known sources nearer if we get to distances from the unknown source which are inconveniently great. The second method requires either a very long room or a means of cutting down the intensity in a known ratio.

We started by trying the first method, but the results were ragged and not satisfactory. To find out why, we compared tungsten lamps, the required voltages of which for equal intensities had been determined by substitution at the same distance from one collimator slit, against another

lamp run at a constant voltage at a constant distance from the other collimator slit. Then we placed the two lamps that were of equal intensity, as shown by substitution in this way, at equal distances from the two slits, and the slits were set at exactly the same opening (determined by calibrating the graduated drums of the slits by a microscope with micrometer eyepiece), all conditions such as slit distances from the cube, etc., being rigidly the same. The fields, however, did not match, which meant that absorption of light through the two collimator systems was not the same, and, though a long series of trials was made, we could not hit upon any ratio of slit widths that would compensate for this so that the light sources could be interchanged. The Physics Department reports the same difficulty with an expensive spectrophotometer recently made for them under the direction of the German Reichsanstalt.

Hence we were forced to fall back on the second method; keeping the tungsten lamp used as constant comparison source at a constant distance from the instrument. The instrument was mounted on a portable stand and the lamp mounted on a rigid bracket attached to the stand. The position of the lamp relative to the slit was thus kept constant. The width of both slits was kept constant (with one unintentional exception to be noted later), the position of the tungsten lamp (a 25 watt rosette type) on its axis was kept constant, the distance from slits to cube was constant; in fact the whole system was kept rigidly the same. Pieces of uniform ground glass were placed before each slit, as otherwise an image of the lamp was formed, and care taken to keep these glasses, the lamp, and cube clean. It would not matter whether the two ground glasses were the same or not, since the method we use makes the absorption in each collimator system immaterial as long as it is the same throughout the series of measurements.

The correct positions of the comparison cube so as to give the same portion of the spectrum from each source was regulated by testing the instrument with sodium flames be-

fore each slit, using the eyepiece, which is removed when we make the fields. If the cube is set correctly, and the collimator tubes are at right angles, the sodium flames will coincide. When this condition has been obtained, the cube is clamped in that position.

The point at which to set the prism system was determined by calibrating the scale over which that system plays by means of the Na, Li, and Tl flames.

TABLE IX

Flame	μ	Scale reading
Tl	0.535	3.50
Na	0.589	3.675
Li	0.671	3.925

Plotting this, we get 3.90 on the scale equal to 0.665 ± 0.005 since the scale divisions were so small that the accuracy of setting was not over two-tenths of a small division. The pointer was set at 3.90 as closely as possible and kept clamped at that point without once disturbing it, throughout the whole series of measurements. Thus λ is kept constant. Whether λ is 0.655, 0.665 or 0.675 does not affect the accuracy of our pyrometer calibrations made from the log x, $\frac{1}{T}$ curve, an iota, but it does affect the value for c_2 deduced from that slope. Since C, the slope of the curve, equals $\frac{c_2}{2\lambda}$ log e, we get, since log e = 0.4343, the following table, assuming different values of λ and of c_2:

TABLE X

Value of C

	$\lambda = 0.660$	$\lambda = 0.065$	$\lambda = 0.670$
$c_2 = 14800$	4854	4818	4797
$c_2 = 14500$	4770	4734	4700
$c_2 = 14200$	4687	4646	4602

We shall come back to this in the discussion of our experimental results.

The constancy of the wave-lengths we are using, then, is assured, but there are several other variables about this type of spectrophotometer that we must look to. The slits move in the collimator tubes and care must be taken to have them exactly perpendicular. The whole instrument must be set up in a straight line with the axis of the temperature tube, which may be attained by sighting across the instrument, by noting the shadow cast on the instrument by the projecting part of the slit holder, and by the use of a translucent screen in front of the slit, by aid of which the instrument may be so set that the slit is in the center of the light spot.

Let us now consider for a moment the comparison light. This was a 25 watt tungsten lamp rated at 112 volts. It was aged at 110 volts for 24 hours, and in use was run at 92 volts. Even carbon lamps aged in this way and then run below their rated voltage remain very constant [19, p. 240] and the tungsten lamp is even better in this respect, since Ives and Woodhull [99] found that after two months daily running for 4 to 7 hours, a tungsten lamp had changed in the voltage required to give 16 c. p., less than two-tenths of one percent.

This assures the constancy of our light source, if kept rigorously at the same voltage. This was taken care of by using an adjustable Rühstrat resistance and a Weston standard portable A. C. and D. C. voltmeter with temperature adjustment, external resistance being put in series with the voltmeter by a resistance box so as to bring the reading for the desired voltage on the most sensitive portion of the scale. A. C. was used simply because the spectrophotometric work was done at night, and the University D. C. went off at 10 P. M., while the A. C. was on till midnight. As the lighting load is not heavy at night, and does not fluctuate greatly, the voltage stayed quite constant, and only slight adjustment of the rheostat was needed.

A second lamp was calibrated, so that the voltage at which to run it gave exactly the same intensity by substitution as the standard, was known, and was kept in reserve against accident to the standard.

The log x, $\frac{1}{T}$ curve was taken with the spectrophotometer on an experimental black body consisting of a graphite plug inside a carbon tube heated in a platinum wound tube furnace. This black body was made up with the same relative dimensions, with graphite diaphragms placed at proportional distances, and in every way as much as possible like the ones pictured in references 19, 22 and 25 in the bibliography. The true temperature of the black body was read by a Pt–Pt 10 percent Rh thermocouple and single pivot galvanometer with zero adjustment. Two such couples were calibrated in a platinum wound furnace to 1470° against a standard couple whose cold junction was kept in melting ice. This couple belongs to the Physics Department and has been calibrated by the Bureau of Standards, so that all our temperature measurements finally rest on this. The temperature of the standard couple was read on a Leeds and Northrup potentiometer. Our two couples were absolutely identical and the deviations from the Bureau of Standards couple were small. A calibration curve was plotted by which all readings were corrected. One of these couples was used throughout the work and the other kept as a secondary standard and the working couple periodically checked against it. The following data (Table XI) and the corresponding points on the lower curve I in Fig. 5 were obtained in the runs on this black body. The distances were measured with a Keuffel and Esser tape. Suffice it to say here that the radiation is shown to be black body radiation within the small limit of error in reading the thermocouple and spectrophotometer.

It is also of interest to note that the temperatures read by the Wanner pyrometer, which is calibrated to read "black body temperatures," [19, p. 231] check the temperature as given

by the thermocouple within the limits of error in setting the pyrometer, as shown in Table XII. This checks the Wanner calibration, as well as our assumption that we are getting practically black body radiation. This Wanner pyrometer had been checked against another which was certified to as correct within 1° at 1000°, 1200°, and 1400°, by the Reichsanstalt, throughout the range over which both were sensitive, and found to agree within the limits of setting:

TABLE XI—WIEN'S LAW CURVE—SPECTROPHOTOMETER ON BLACK BODY IN PLATINUM-WOUND FURNACE

Distance x in inches	Temp. degrees abs. by thermocouple	Log x	$\frac{1}{T} \cdot 10^{-4}$
	Run of Dec. 5.		
53.2	1628	1.726	614
59.0	1662	1.771	602
61.5	1668	1.789	600
56.0	1643	1.748	609
54.2	1633	1.740	612
47.0	1613	1.672	620
42.5	1581	1.628	632
38.4	1562	1.584	640
35.3	1527	1.548	655
31.9	1497	1.504	667
28.1	1478	1.447	677
24.3	1445	1.386	692
20.2	1395	1.305	717
	Run of Dec. 6.		
24.4	1425	1.387	699
27.2	1450	1.435	690
30.1	1475	1.478	678
33.2	1498	1.521	667
39.1	1531	1.592	653
43.0	1559	1.663	641
47.8	1585	1.679	631
53.0	1609	1.724	622
60.1	1653	1.779	605
65.7	1667	1.818	600
70.4	1683	1.848	594
80.0	1715	1.903	583

With the slit width used (1.80 on the drum) the field was so faint at first that accurate settings could not be made below 1122° C (1395° Abs.). A wider slit would have meant inconvenient distances at very high temperatures. For fear of injuring the platinum wound furnace the highest point taken was 1442° C (1715° Abs.).

Day and Sosman [33, p. 148] have shown that the thermocouple temperature scale, as usually given by extrapolation above the copper point, leads to low results at the higher temperatures as compared with the nitrogen thermometer, and Waidner [18, p. 55] gives a correction table.

The results here given have not been corrected, since the Bureau of Standards calibration of the standard couple may have been made on the basis of their 1546° determination of the melting point of Pd, which is in fair accord with the results of Day and Sosman. If the corrections were applied, they would change the slope of the curve but slightly, and what change would be made would be in the direction of a lower value for the slope, and hence a lower value for c_2 of the Wien equation, and would tend to show an even more complete approach to black body radiation from our temperature tube.

TABLE XII—TEMPERATURES OF BLACK BODY IN PLATINUM FURNACE

By thermocouple	By Wanner
1165°	1167°
1200	1205
1238	1236
1280	1276
1321	1323
1324	1318
1345	1341
1370	1367
1375	1378
1430	1427

The thermocouple was in a porcelain protection tube which was inserted into a hole bored in the graphite plug.

The position of plug and couple could be varied by several centimeters inside the furnace without changing the reading of the couple, hence the results are not open to the criticism we made on Lampen's.

One run was made with the bare couple inserted in a tiny hole in the plug. Agreement of couple and Wanner was good up to about 1200°, when carbide was formed in the couple, and the readings became erroneous and the couple brittle. The couple was cut off back of the crystallized position, fused together in the oxyhydrogen blast, the resistance of couple and leads again adjusted to the proper value, the couple annealed at white heat by an electric current and the couple again calibrated against the secondary standard, when it gave the same readings as before.

It is worthy of note that in this run the platinum was at no time visible against the graphite, showing that we had practically a uniformly heated enclosure.

The data on the platinum furnace are necessary to give the distance corresponding to known temperatures with the spectrophotometer, and also give information on the slope of the Wien's law curve and the value of c_2. The next step is to get a similar curve for the regular temperature tube. Comparison of the two slopes will show the deviation from black body radiation of our tube.

In the work with the regular tube, the crux is really to determine the true temperature of the surface of the plug. (Compare abstract of report of work of Reichsanstalt for 1908 [70]. First we tried inserting a porcelain pyrometer tube 2 mm thick between the two tubes shown in Fig. 2, cutting in the plug to receive the end of the tube, a recess of such depth that the junction of the couple was just at the level of the surface of the plug. With this arrangement the Wanner read from 50° to 150° higher than the couple, the difference decreasing as the temperature rose. Now the "black body" temperature shown by the Wanner cannot be higher than the actual temperature, since that would mean that the body was giving more than black body radiation, an

impossibility; hence the trouble is due to the slow heat conductivity of porcelain, with consequently too great a drop in temperature through the porcelain.

The next attempt was made by grinding down the end of the porcelain tube to a thickness of 0.4 mm. This was then placed tightly against the plug, in a depression 0.4 mm deep, and the thermo junction made very small, to allow close contact with the porcelain, and thus prevent lag. This gave somewhat better results than before, but the readings of the couple were still too low.

Though these Berlin porcelain tubes do not soften appreciably throughout at 1600°, they showed a fusion of the glaze at between 1200° and 1400°, so that the junction became embedded in the glaze, and the tube had to be broken to get the couple out. This was remedied by putting a tiny pinch of pure Al_2O_3 in the porcelain tube before inserting the couple, so as to get a dust of Al_2O_3 over the inner surface of the tube, and keep the junction from actual contact with the glaze.

An attempt was next made to determine the temperature of the back of the plug by inserting it in a bath of copper, as shown in Fig. 4, and taking the temperature of the copper with a thermocouple.

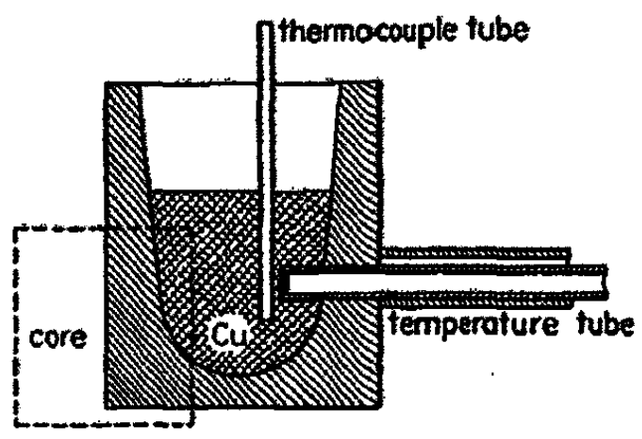

Fig. 4.—Copper Bath for Black Body Radiation.

The crucible was turned out of Acheson graphite and fitted with the usual inner tube, as shown. Outside the crucible the usual outer tube was fitted on. The crucible was placed in a resistance furnace for crucibles with a granular

carbon core, after the style of the furnace recommended by Fitz Gerald[71] and Tucker,[72] and heated. It was necessary to place the core as shown by the dotted square in Fig. 4, as otherwise the crucible itself formed too great a part of the resistor, and its walls got hotter than the contents, giving us a tube having a temperature gradient with a hump in it.

By heating slowly and stirring the copper we can get the temperature of the inside surface of the plug, and by using plugs of known thickness and proceeding as was done in the work on the temperature drop through the plug in the regular tube, we can extrapolate back and find the temperature drop through the plug from copper to open air. This was done, and for temperatures of 1083° and 1133° it was found that the extrapolated temperatures of the back of the plug, determined by the Wanner, and the true temperature as shown by the thermocouple, checked within less than five degrees, or as close as the Wanner could be read. This shows that we have practically black body conditions in this tube. But we have more ideal conditions as to uniformity of heating of the cavity right around the plug, and the temperature gradient right at the plug is not so steep. Besides this, we have the uncertainty of an extrapolation. Hence the results are not conclusive for the regular tube.

We got 1083° for the melting point of pure electrolytic copper, against the usual value of 1084°—and that of Day and Sosman, 1082.6°,[33] thus checking our thermocouple calibration nicely. The cold junction of the thermocouple, with this arrangement, was near the furnace, and to keep it and the leads and galvanometer at uniform temperature, the couple and leads were threaded through a condenser bearing a thermometer. Cooling water was then run through the condenser at such a rate as to keep the thermometer in contact with the cold junction inside, and one at the galvanometer, at the same temperature, which could then be used in correcting the thermocouple back to the cold junction temperature used in calibration.

In using the crucible with the inserted tube it is neces-

sary to pour out the copper while still molten, since if it solidifies, the crucible splits in two, because the expansion before melting in the next heat is so great, and because free motion is prevented by the projecting tube.

The next step was to try a platinum plug in the end of a porcelain tube inserted between the outer and inner tubes of the regular temperature tube, instead of one of solid porcelain. A porcelain tube open at both ends was tightly fitted with a little platinum cup made of foil 0.2 mm thick, so shaped as to give a flat platinum diaphragm at the end of the tube. The tube was so inserted that the platinum rested tightly against the plug, and the thermojunction was then pressed tightly against the platinum. Save for the drop in temperature through 0.2 mm. of platinum, which should be negligible, we thus measure the actual temperature of the surface of the plug.

It was recognized that the platinum cup, being in contact with the graphite, would form carbide; and since the platinum cup could not be fitted in gas tight, it was expected that the reducing atmosphere present would injure the couple, hence it was planned to use a new platinum cup for each run, and to check the thermocouple after each run.

The first run went beautifully, the following data being obtained on the relation between temperatures as read by the Wanner, and by the thermocouple.

TABLE XII—REGULAR TEMPERATURE TUBE

Temperature by thermocouple	Temperature by Wanner
963°	959°
982	986
996	996
1000	1005
1071	1073
1198	1198
1285	1284
1306	1304
1397	1396
1435	1441
1473	1472
1510	1516

Since the Wanner reads black body temperatures, and the couple, disregarding the drop through the platinum, the true temperatures, we see that the deviation from black body radiation is entirely negligible.

A few points were taken with the spectrophotometer on this run, the data for which are given at the beginning of Table XIV, under "Run of Dec. 28," and are plotted on the upper curve (II) in Fig. 5. It will be noted that the slope of this line and that of curve (I), the lower portion of which is plotted from data taken on the black body in the platinum-wound furnace, is exactly the same, but that this line lies above the others. On hunting for the cause of this, it was found that, most unfortunately, the drum that regulates the slit width of the slit receiving radiation from the temperature tube, being rather loose in its bearings, had moved in moving the instrument. On checking up the settings of the slits, as was done before each run, and continually during the run, it was found that the drum had been set back, after its displacement, to 2.800 instead of 1.800. That is, two and eight-tenths revolutions of the drum had been made instead of one and eight-tenths. This will not affect the slope of the $\log x$, $\frac{1}{T}$ curve at all, but only the intercept, hence the agreement between the slopes of the two curves really shows as well that our tube is actually giving black body radiation, as it would if the points lay on the first curve, though it is not quite so pretty a proof.

After this run the thermocouple was checked in freezing copper, and gave 1083°. Hence it has not been affected by carbide formation, and our results are trustworthy. The platinum cup was crystalline and brittle, showing carbide formation. This, however, had not extended clear through the cup, the inner surface, next the junction, being smooth and uncrystallized.

We then attempted to duplicate this run, and get points for our curve with the proper opening of the spectrophotometer slit, but in three trials we were unable to finish a run without carbide formation in the couple and consequent

invalidation of the readings. With this we stopped the work on the question of deviation from black body radiation, and began to compare the temperatures shown by matching the spectrophotometer field when set at the proper distance from the hot body to give some definite temperature, taken from the extrapolated log x, $\frac{1}{T}$ curve, with the readings of the Wanner pyrometer, up to 2600° C. We shall deal further with these data under the discussion of the pyrometer, but since the spectrophotometer readings and those of the pyrometer agreed satisfactorily over the entire range, they show that, if we assume the correctness of our extrapolation, the pyrometer calibration was correct; or if we assume the pyrometer correct, it checks our Wien's law curve over the range from 1200° to 2600°, as being the continuation of the one obtained on a black body in the platinum furnace, when the temperatures were measured by a thermocouple over the range 1120° to 1450°. Since compensating errors would hardly balance things up through this range, it is likely that both assumptions are correct.

TABLE XIV—DATA FOR LOG x, $\frac{1}{T}$ CURVE, REGULAR TEMPERATURE TUBE

Run of Dec. 28

x inches	T abs.	log x	$\frac{1}{T} x$ 10^{-4}
32.5	1370	1.512	730
32.5	1378	1.512	729
37.3	1387	1.572	719
191.0	1789[1]	2.281	539
19.2	1268	1.284	789
19.7	1276	1.295	784
29.6	1343	1.471	745
39.3	1384	1.511	722
55.5	1481	1.744	675
148.5	1708	2.172	585

[1] First four readings made with Wanner alone. The rest by thermocouple in platinum tipped porcelain tube and checked by Wanner readings. See Table XIII.

Spectrophotometer slit at 2.800. Plotted on upper curve (II). Fig. V.

TABLE XIV—(*Continued*)

x inches	T abs.	log x	$\frac{1}{T} x\ 10^{-4}$
Run of Jan. 2			
39.8	1565	1.600	639
26.8	1443	1.428	693
35.9	1503	1.555	665
47.2	1573	1.674	636
67.2	1663	1.827	601
90.3	1743	1.956	574
218.0	2053[1]	2.337	487
Run of Jan. 3			
29.0	1454	1.462	688
36.2	1503	1.559	665
45.7	1565	1.660	639
59.7	1640	1.776	610
60.4	1675	1.781	597
80.2	1714	1.904	584
155.5	1945	2.192	514
184.0	2001	2.265	500
218.0	2053[1]	2.337	487
Run of Jan. 8[2]			
306.6	2183	2.486	458
319.6	2218[1]	2.505	450
319.6	2200	2.505	455
397.6	2306[1]	2.599	434
397.6	2333	2.599	429
Run of Jan. 9[2]			
226.5	2030	2.355	493
497.5	2498[1]	2.697	400
586.0	2581	2.768	387
344.0	2290	2.537	437
206.0	2083	2.314	480
Run of Jan. 11[2]			
700.0	2673	2.845	374
795.0	2778	2.900	361
795.0	2788[1]	2.900	359

Spectrophotometer slit at 1.800.

Temperature read by Wanner.

[1] Temperatures measured by Wanner with dark glass K = 2586.

[2] Temperatures read by Wanner with dark glass K = 205 unless otherwise noted.

Distances measured with aid of rotating section or disk, K = 25.

TABLE XV

Log x, $\frac{1}{T}$ curve

Spectrophotometer set at proper distance to give, from extrapolated curve	Temp. read by Wanner	Log x	$\frac{1}{T}$ x 10^{-4} from Wanner readings
1200° C	1209° C	1.435	675
1300	1300	1.718	636
1400	1402	1.812	597
1500	1507	1.966	562
1600	1615	2.147	530
1700	1705	2.240	506
1800	1800	2.345	482
1900	1900	2.447	460
2000	2005	2.540	439
2100	2100	2.625	421
2200	2200	2.705	405
2300	2300	2.777	389
2400	2410	2.850	372

The slope of both curves in Fig. 5 is 4600 ± 30. Comparing this with Table IX, we see that it indicates that either for $\lambda = 0.665$ at which we tried to set the spectrophotometer, or for $\lambda = 0.670$ which we might have had, owing to the difficulty of setting the instrument exactly, the value for the constant c_2 of the Wien equation must be nearer 14200 than the usually accepted value of 14500. This checks with the Holborn and Valentiner figure of 14200 ± 1 percent.

Owing to the difficulty of mantaining the regular furnace at a constant temperature throughout the reading of both spectrophotometer and Wanner, and on account of the impossibility of accurately determining λ with this spectrophotometer, and the many variables affecting this form of the instrument, our results are not to be taken as conclusive on the value of c_2. However, since it is certain that the more perfect the black body the lower the value of c_2, our results have led us to adopt the Holborn and Valentiner figure of 14200 in all calculations based on Wien's law throughout this paper.

Though our work cannot attain to the dignity of a new determination of c_2, yet it proves conclusively the point we wished to establish, that the temperature tube gives practically black body radiation, so that no correction for deviation is necessary. Were we on the other side of 14500, say at 14800, we should fear deviation from the condition of a complete radiation, but at 14200 we are certainly getting negligible deviation from black body radiation for pyrom-

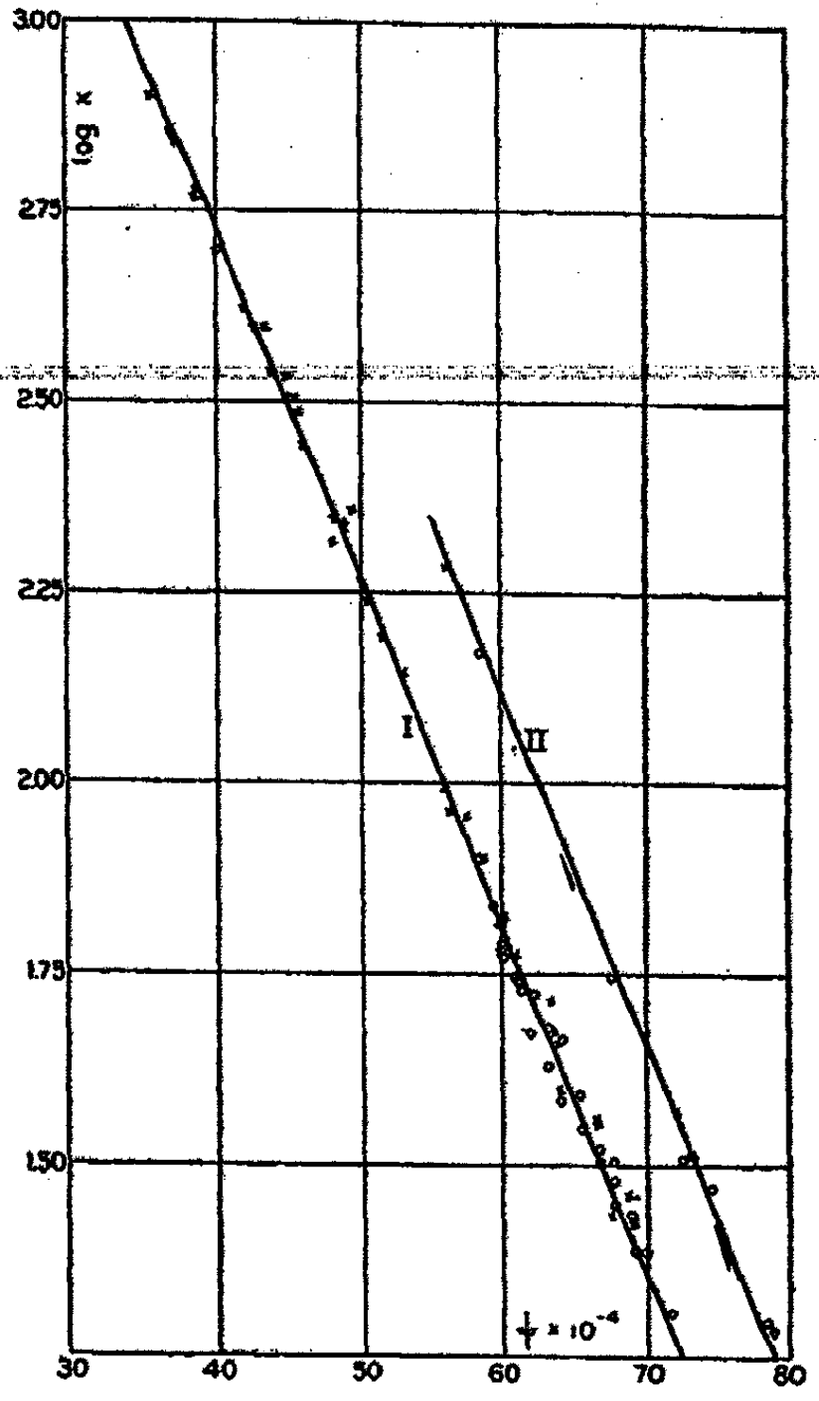

Fig. 5.—Wien's Law Curve. Crosses denote temperatures read by Wanner pyrometer. Circles denote temperature read by thermocouple.

eters like the Wanner, which use red light. It will be shown later that the same is true for total radiation pyrometers.

To sum up the factors affecting temperature measurements made in our double-walled carborundum tube, we have seen that the tube has such a temperature gradient in respect to the furnace gradient, as to give practically correct readings; that the plug under normal conditions is uniformly heated; that the difference in temperature between the two surfaces of the plug may be approximately corrected for at any given temperature, and such corrections have been obtained; that the use of suction to sweep out the fumes introduces no measurable error; and that the deviation from black body radiation is negligible. Above all, the fume difficulties have been minimized.

Having covered the question of the tube, let us now turn our attention to the pyrometers employed, and their calibration from 1200° to 2600° or above.

Three types of pyrometers were available for this work, the Wanner, the Morse, and the Thwing.

The Wanner used throughout the work was a very good instrument of recent manufacture, belonging to the Department of Physics. For diagrams and descriptions of this instrument see references 15, p. 72; 19, p. 229; 22, p. 226; 37, p. 462, in the bibliography. The Chemical Department owns a Wanner of earlier date, put out, in fact, before the necessity of keeping the current passing through the comparison lamp constant by means of a voltmeter or ammeter, was realized. This has a Reichsanstalt certificate showing it to be correct within 1° at 1000°, 1200°, and 1400°. When used above 1600°, however, it does not give the same color of object and comparison fields, while the Physics instrument does not show this fault till well above 1800°. Throughout the 1000°–1400° range, the two instruments agree within 5°, or to the error of setting.

In using either instrument the current was kept constant at the value found to give the proper "normal number" against the standard Hefner amylacetate lamp, by means of

an ammeter or voltmeter, and adjustable resistance. Cf. reference 19, p. 229. The instrument was always used normal to the hot surface, to prevent errors due to polarization [19, p. 235].

The Chemical Department Wanner is not provided with a dark glass for a higher temperature range; the other is. However, on plotting for the Physics instrument, scale readings against the temperatures from the calibration table, it is found that either with or without the dark glass the instrument is quite insensitive between 1750° and 2100°. Fig. 6,

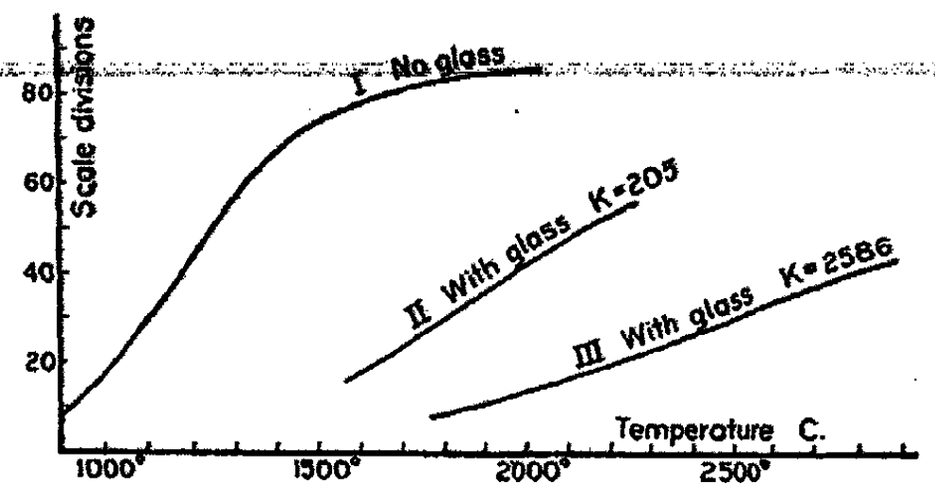

Fig. 6.—Calibration Curves. Wanner Pyrometer.

Curve I, shows the curves for the instrument without any dark glass, and Curve III that with the dark glass supplied with the instrument. Since the formation temperature of carborundum, which we wish to determine, lies in this range, the Wanner as it stands, is not satisfactory. The use of the dark glass to cut down the intensity of light from the hot source, thus allowing reading of higher temperatures, depends on another application of Wien's law. If we insert a dark glass, an absorbing mirror, or a rotating sector disk in the path of the light from the hot body, we cut down the intensity in some certain ratio, which ratio is the coefficient of absorption of the absorbing medium used.

Since

$$\frac{I_o}{I_1} = \frac{x_o^2}{x_1^2} = e^{c_2 \eta \lambda \left(\frac{1}{T_1} - \frac{1}{T_o}\right)}$$

the ratio $\frac{I_o}{I_1}$ is the coefficient of absorption, K, and if T_o is

the true temperature, then T_1 is the apparent temperature when the absorbing medium is interposed.

Then we have

$$\log \frac{I_o}{I_1} = \log \frac{{x_o}^2}{{x_1}^2} = \frac{c_2}{\lambda} \log e \left(\frac{1}{T_o} - \frac{1}{T_1} \right)$$

Hence if we once determine the coefficient of absorption, K, we can figure back to the true temperature corresponding to the Wanner reading obtained with it. Figuring from the Wanner tables, we find for the dark glass supplied with the Wanner (Fig. 6, Curve III) that K = 2586 if c_2 = 14200, or 3000 if c_2 = 14500, for λ = 0.656μ.

Then if we use a glass of the proper absorption power, lower than 2586, we should be able to obtain such a curve as II, Fig. 6, when the most accurate readings lie in the 1800°–2250° range we wish to use hereafter.

The absorption factor of such a glass may be determined by the spectrophotometer, since $K = \frac{{x_o}^2}{{x_1}^2}$ where x_o is the distance corresponding to the true temperature T_o, and x_1 the distance corresponding to the apparent temperature T_1, to the equivalent of which the radiation from the body at T_o is cut down by the interposition of the glass. K should of course be determined, using the same wave-length of light in the spectrophotometer as will be used in the pyrometer to which the glass is to be applied, since most glasses show some selective absorption.

On attempting to determine K for the dark glass supplied with the Morse instrument so as to be able to use that glass with the Wanner, it was found that, in order to get a large enough x_1 to allow accurate setting of the spectrophotometer, x_o was too great for the length of the room. This same difficulty had to be overcome in working above 1700° in getting Fig. 5. Hence some absorbing medium, with a rather low and accurately known coefficient of absorption is needed, so that by its use we may cut down x_o to a reasonable figure.

Waidner and Burgess[25] and Hyde[78] have shown that the rotating sector disk may be used for this purpose, and that it has the advantage that K may be determined by measurement of the angle of the sector opening as well as by the spectrophotometer. For instance, one made with an opening of 14.4° gives K = 25, and the distances measured with it are just one-fifth of those measured without it. One 15 inches in diameter was made up with this opening, from thin sheet metal, painted dull black. It was rotated by an 1800 R.P.M. motor. This speed was rapid enough to prevent flicker. By the spectrophotometer, two determinations of K gave 24.9 and 25.1.

By sighting a spectrophotometer on a black body whose temperature was known, by thermocouple or otherwise at a couple of temperatures, and measuring the corresponding distances, and thereafter setting the instrument at a fixed distance from the body whose temperature is to be measured, it would be possible to calculate from Wien's law the distances required for any other higher temperature. Then these distances could be calculated over, so that we knew the opening of a sector disk which would have to be interposed, so as to make the distance at which the spectrophotometer was set, equivalent to any greater distance, An adjustable sector disk, such as is shown by Fleming (66, p. 171) could be used, and the temperatures corresponding to different equivalent distances, *i. e.*, to different openings of the sector, could be placed on the scale over which the lever that governs the size of the sector opening, plays. Thus a laboratory having a spectrophotometer, but no optical pyrometer, could improvise a usable direct reading pyrometer for laboratory investigations.

Now having our rotating sector, we are in a position to get the absorption of our dark glass. Using the spectrophotometer, we got 204, 205, 200, 198. By taking readings with the Wanner with and without the glass, and using $c_2 = 14200$, we got 207, 208, 201. Hence we may take 205 as the value for this glass. It was impossible to make a determination

on the dark glass originally supplied with the Wanner, as it was too small to cover the spectrophotometer slit.

Using this value of K for our dark glass, a table was made on the basis of Wien's law, which gives the values plotted on Curve II, of Fig. 6. Comparative readings on the Wanner with no glass and with this glass, or with this glass and with the origina one, taken at points where the curves overlap, agree within the limits of error in setting the instrument. Thus we have made the Wanner sensitive to about 10° C over the range we wish to measure.

The principle of the disappearing filament used in the Morse thermogage is described by Chwolson [5, p. 77], Waidner and Burgess [22, p. 213], LeChatelier [19, p. 241], Iklé [37, p. 463] and Waidner [18, p. 52]. While the principle is properly stated, Waidner and Burgess say that Morse uses a large spiral filament which is hard to match, that the pyrometer demands too high a voltage (40–60), has no focussing device, needs red glasses before the eye and a dark glass before the filament, for high temperatures. Burgess [19, p. 237] condemns it for use above 1200°, though in the work at the Bureau of Standards under his direction, as for instance that on the melting point of platinum,[25] they continually use what they call the Holborn-Kurlbaum pyrometer. This is simply the German form of the Morse instrument; it is manufactured under the Morse patent and can only be obtained in this country from the Morse Thermogage Co. Save for the use of absorbing mirrors instead of dark glass, and for a slightly more compact form, it differs in no essential form from the Morse instrument. Since Morse defeated Siemens and Halske, who were making the Holborn-Kurlbaum instrument, in the patent litigation in Germany (see Waidner and Burgess (22, insert slip p. 233) and Iklé (37, p. 463, footnote)) it only seems right to give him the credit that is his due, more particularly as each and every point criticized by Waidner and Burgess in earlier papers, and passed over in silence in later ones, has been attended to in the modern Morse in-

strument, and Waidner and Burgess must have been aware of the improvements.

In the latest form it uses a 6-volt tungsten lamp with a simple W-shaped filament; the instrument is a telescope and may be focused for object and filament; both red and dark glasses are provided and when properly calibrated, it may be used with good results up to 2500° C. By the use of a still thicker dark glasses the range might be extended to the highest attainable temperatures.

In the earlier part of this work, a Morse instrument belonging to the Department of Physics was used, but its dark glass was not dark enough to allow us to go as high as we wished. Moreover, at about 1700°, according to the calibration of this instrument, a point was reached at which a considerable increase in current gave but little increase in brightness of the filament, thus making settings uncertain.

The second instrument was made up with a specially thick dark glass, and loaned by Mr. Morse to Prof. Bancroft for this work.

We procured a special Weston laboratory standard milliammeter for use with this pyrometer, having a 12-inch scale for 2000 milliamperes, thus allowing very delicate readings.

We made a calibration curve for the Morse instrument, plotting milliamperes passing through the lamp against temperature of the hot body as shown by the spectrophotometer. Morse's calibration was seen at once to give too low readings if we took the brighter part of the filament, so we used the darker side, since the illustration on the calibration sheet showing the part of the filament to use, might be taken to mean either side of the filament, according to which way the lamp was faced. Using the darker side, we found Morse's calibration for the dark glass low by 30° at 1200°, the deviation growing less up to 1800°. From that point up the agreement was very close. The calibration thus obtained against the spectrophotometer was the one used in the measurement of the formation and decomposition temperatures of carborundum recorded later in this paper.

On communicating our results to Mr. Morse, we found that the brighter side of the filament was the one that was supposed to be used. Then, using that part of the filament, we took the calibration of the instrument up to 1320° C on a black body in a platinum furnace, measuring temperatures by the thermocouple and then in the regular form of temperature tube in the regular carborundum furnace from that point up to 2500°, reading temperatures by the Wanner.

Over the 900°–1200° range our figures for the instrument without either dark or red glasses, agreed well with those furnished by Morse, our values averaging about 5° higher. 1200° is as high as readings can be made without the red glasses. With the red glasses, but no dark glass, the range is extended to over 1400°. Morse did not furnish a calibration corresponding to this.

With both red and dark glasses, using the bright side of the filament, we found Morse's calibration 120° low at 1130°, the deviation growing less at higher temperatures until at 2475° his values were correct within the errors of observation. The data are given in Table XVI and our calibration curve is given in Fig. 7:

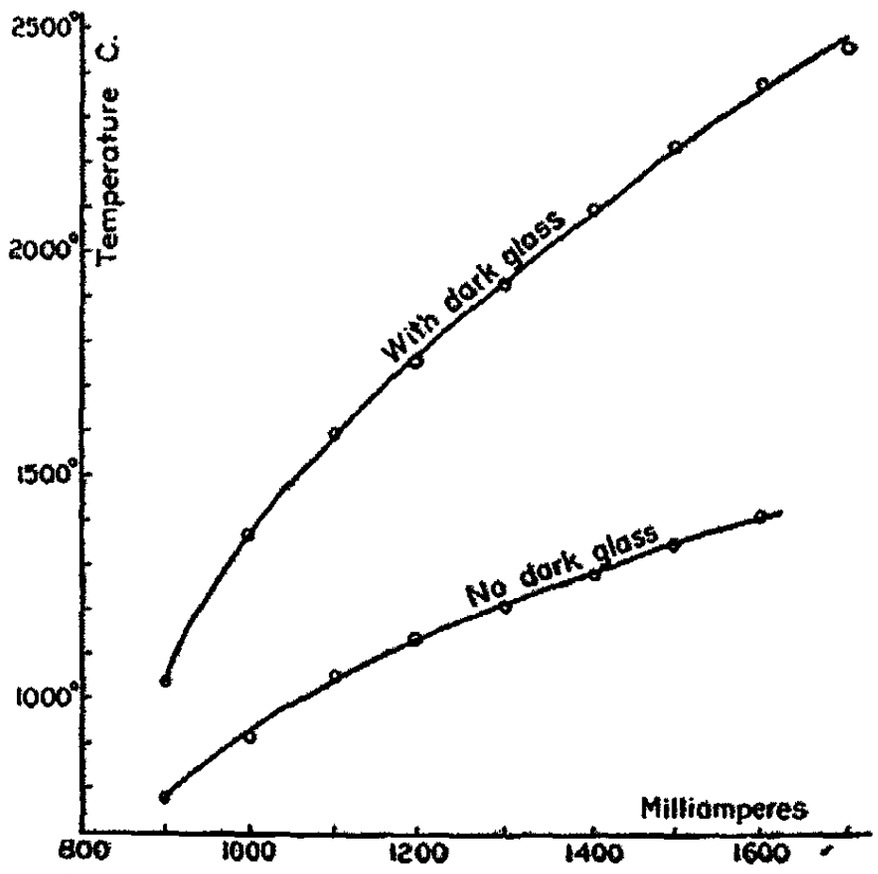

Fig. 7.—Calibration Curves. Morse Pyrometer.

TABLE XVI—MORSE PYROMETER

Milli-amperes	Degrees centigrade red glasses, no dark glass	Degrees centi-grade red and dark glasses	Degrees centi-grade Morse calibration red and dark glasses	$\frac{1}{T_0} - \frac{1}{T_1}$
900	700	1130	1010	0.000246
1000	910	1360	1320	0.000233
1100	1045	1590	1540	0.000233
1200	1130	1760	1740	0.000221
1300	1200	1930	1920	0.000225
1400	1280	2100	2090	0.000223
1500	1345	2240	2250	0.000220
1600	1410	2385	2388	0.000218
1700	....	2475	2470	.....

The last column gives $\frac{1}{T_0} - \frac{1}{T_1}$, where T_0 is the absolute temperature of the hot body for a given current through the lamp without the dark glass, and T_1 the temperature for the same current with it. We have already seen that where Wien's law strictly applies, the value is a constant. The reason it is not constant here is because, unlike the Wanner, which is a spectroscopic instrument, the red glasses used in the Morse are not wholly monochromatic, but admit a band of light. This can be readily seen by viewing the lithium and sodium flames through the red glasses, the sodium flame being almost as bright as the lithium.

Now we know that the wave-length corresponding to maximum light intensity, shifts, with rising temperature of the luminous source, towards the shorter wave-lengths. Waidner and Burgess [22. p. 201] plot curves showing this. Watson[74] explains how the red is the first light to appear on heating a body, the yellow beginning to appear at about 1000°, while at 1600° the light is practically white. This shift from the red to the violet end of the spectrum of the light emitted from a hot body was very noticeable on our regular temperature tubes at temperatures of 2500°–2600° C, as the light emitted was distinctly greenish; so much so that people coming into the room, and seeing it reflected

from the walls opposite the tube, would comment on its green color at once.

Using the value 205 for the absorption coefficient of our dark glass and substituting the observed values of $\frac{1}{T_o} - \frac{1}{T_1}$ in the Wien equation,

$$\log K = \frac{c_2}{\lambda} \log e \left(\frac{1}{T_o} - \frac{1}{T_1} \right)$$

we find that at 1130° our effective wave length is about 0.65μ, while for 2475° it is about 0.59μ. This is checked by the fact that the impression the eye receives on looking into the eyepiece of the pyrometer at the highest temperatures is that of a distinctly yellowish color. This does not agree with the results obtained by Waidner and Burgess [25, p. 176] where they found the position of the maximum of intensity as viewed through a red glass, to shift towards *longer* wave lengths over the range 1000°–1450°. Whether this is due to a difference in the nature of the red glasses used by them and by us, we cannot say, but it seems strange that they should find that the maximum of intensity viewed through a certain glass shifts in exactly the opposite direction from that in which the maximum of intensity is really shifting in the spectrum of the hot body.

In order to find out how the values in the Morse calibration table supplied with the instrument were obtained, we took the matter up with Mr. Morse. After ageing his lamp for 24 hours at a voltage above the highest at which it will be used, he calibrates the instrument without dark or red glasses, using an electrically heated hot body, against another Morse pyrometer whose calibration is known. Then, reading the temperatures with the standard instrument, he takes three readings with the instrument to be calibrated, using the red and dark glasses. He then takes the current through the lamp, corresponding to each of these three readings and from his calibration curve without the dark or red glasses, finds the temperature there corresponding to those values of the current. Then he has three pairs of temperature read-

ings, each pair for the same current, with and without the glasses. He then plots temperatures with the glasses against those without, draws a straight line through the three points, and then takes from this straight line the temperatures with the glasses, corresponding to those without. He states that he always finds these three to lie on a straight line when plotted this way.

Now this corresponds to the assumption that $T_o = KT_1$, whereas according to the Wien equation, the relation is $\frac{1}{T_o} - \frac{1}{T_1} = K$. The only way that Morse's assumption can be approximately true, is to have, by good luck, a red glass through which the effective wave-length shifts with the shifting of the maximum of intensity, just enough to compensate for the difference in the two formulae.

For temperatures from 1900° to 2500°, as Table XVI shows, this happy accident has occurred. Were this not the case, and we had $\lambda = 0.65\mu$ at 2475°, as at 1130°, $\frac{1}{T_o} - \frac{1}{T_1}$ would then equal 0.000246 as at 1130° and the pyrometer would indicate 2760°, on the basis of Morse's calibration, or 300° too high.

The set of readings taken by Morse in the calibration of the pyrometer lamp used in our instrument is given below:

TABLE XVII

No glasses		With dark and red glasses		$\frac{1}{T_o} - \frac{1}{T_1}$
°F	°C	°F	°C	
1561	855	2122	1167	0.000194
1628	892	2252	1237	0.000216
1686	925	2374	1305	0.000273

The value of $\frac{1}{T_o} - \frac{1}{T_1}$ which we have calculated from his figures shifts in the opposite direction from that in our set of readings. However, figuring the corresponding wave length of the effective light from the Wien equation for his values

at 1167°, we find $\lambda = 0.52\mu$, which is in the green, and we do not believe that at 1167° the displacement of the maximum of intensity will force green rays through a red glass. The difficulty of making accurate readings at the low intensity corresponding to 1167° with the dark glass, is great, and may account for much of his error.

Since the calibration provided by Morse without the dark or red glasses *only* goes up to 1220 milliamperes, or 1140°, he has to extrapolate the current-temperature curve (which is a curve and not a straight line, see Fig. 7) before he can take the corresponding temperatures with the glasses that correspond to current values above 1220 milliamperes. Errors in this extrapolation may also have aided in compensating for the error due to his assumption that the relation is $T_o = KT_1$. It will be noted that the values for T_o and T_1 from Table XVI do not lie on a straight line.

We therefore think that the Morse calibration for the instrument with the dark glass is based on an erroneous assumption, and that the almost complete compensatism for this error, which brings his values out so nearly correct at higher temperatures, may be traced to the shift in the effective wave-length of light, due to lack of monochromatism in the red glasses.

While a Morse pyrometer for high temperatures ought to be calibrated against a spectrophotometer, or at least a Wanner, in order to make certain that readings are giving actual as well as merely reproducible temperatures, one so calibrated is satisfactory for high temperature work, and has the very great advantage for work with experimental electric furnaces that it demands the smallest hot body of any high temperature pyrometer known, and hence large temperature tubes may be dispensed with.

We think that the Morse instrument might be vastly improved by adding a collimator slit, and a prism between the eye and the lamp so that the field be illuminated by monochromatic light, as is the case with the Wanner. Wien's law would then be strictly applicable, and calibration of

the instrument for high ranges by the use of absorption glasses would not be complicated by the shift of the maximum of intensity and would rest on a sound theoretical basis. To avoid any danger of selective absorption in the dark glass, a rotating sector of small opening might be used, which would have the advantage of allowing a determination of the coefficient of absorption by calculation from the angular opening as well as by direct determination. The rotating sector would hardly be practicable for a commercial instrument, since the vibration might jar the filament too much, though in the Ives colorimeter a rotating color mixer is used that runs with almost no vibration. (See note at end of bibliography.)

For measurements at 1800°–2600°, radiation pyrometers of the Féry or Thwing type, seemed very promising. With optical pyrometers like the Wanner or Morse, it is necessary to cut down the intensity so much by absorbing glasses that we vastly reduce the delicacy of our readings. With radiation pyrometers, the scale readings for a given temperature increment, increases with increasing temperature, *i. e.*, the higher we go the more delicate our readings.

A Féry instrument was tried out by one of their salesmen in comparison with the Wanner and the Morse belonging to the Physics Department. All these were sighted on a graphite plug 1″ in diameter at the end of a 12″ elbow form temperature tube. The following temperatures were read:

Wanner	Morse	Féry
1596° C	1605° C	1450° C
2010	1810	1910

The higher temperature was above the point where this Morse instrument was known to be inaccurate, hence the lack of agreement there is not surprising. That the Féry gave low readings showed that the hot body was too small to cover the field entirely at that distance. It was figured that a 3″ plug would not have been much too large. The Féry

readings were consistent, and could be duplicated to a remarkable degree of exactness.

The large size of the hot body needed, while not a vital fault in many industrial operations, throws the Féry out of consideration as a laboratory instrument, for to get a field 3″ in diameter in our form of temperature tube, the outer tube would have to be about $4^1/_2$″ in diameter, and to get uniform heating of the plug, and to keep the volume occupied by the tube from being too large a percentage of the total furnace volume, we would have to enlarge our experimental furnaces to unwieldy sizes.

While the Féry could probably be modified to meet our special conditions, its price is prohibitive even without any special modifications.

Hence we turned our attention to the Thwing pyrometer. Our conditions were rather unusual. We wished to use a small field, and yet to get a high degree of accuracy at temperatures far above the usual range for which high temperature pyrometers are used. Dr. Thwing took up the problem and furnished several pyrometers, each of which was tested in turn, criticised and reported on. Using the facts thus discovered, Dr. Thwing would modify the pyrometer accordingly.

The commercial form of the instrument consists of a 1″ metal tube about 3′ long, at one end of which may be inserted diaphragms of various sizes. Near the other end is an aluminum cone about 4″ long, $^7/_8$″ diam. at the larger end and $^1/_8$″ at the smaller, open at both ends. This serves the same purpose as the parabolic mirror in the Féry instrument; it acts as a sort of funnel, receiving the radiation from the hot body and concentrating it, by multiple reflection, on the hot junction of a tiny thermocouple placed behind the smaller end of the open cone. This couple is very thin, only about $^1/_{1000}$ inch in thickness, to allow it to assume equilibrium rapidly, and to insure a rapid return to zero reading on the galvanometer when the radiation is cut off. Its composition being a trade secret with Dr. Thwing, we were told

only that the wires were nickel alloys. The nickel-nichrome couple is finding considerable use nowadays but whether chromium enters into the composition of either element of the couple we do not know. The e.m.f. produced by the heating of this couple from the total radiation falling on it from the hot body is read on a delicate portable galvanometer, corrected for temperature changes by an ingenious device.

Since the intensity of radiation varies as the square of the distance from the hot body, and since the area of the spot of light admitted by the diaphragm also varies as the square of the distance, the pyrometer is independent of its distance from the hot body as long as the body is large enough so that at the farthest distance it completely fills the angle substituted by the diaphragm. A diagram of the commercial instrument is shown by Waidner [18, p. 52].

The commercial instrument needs slightly too large a hot body to be applicable to our work, in which we did not wish to use a hot body larger than 1″ in diameter nor to put the pyrometer closer than 18″ from the radiating source. To meet our conditions, Dr. Thwing used a Leeds and Northrup wall galvanometer, the sensibility and resistance of which could be varied by a device shown in Fig. 8. This also

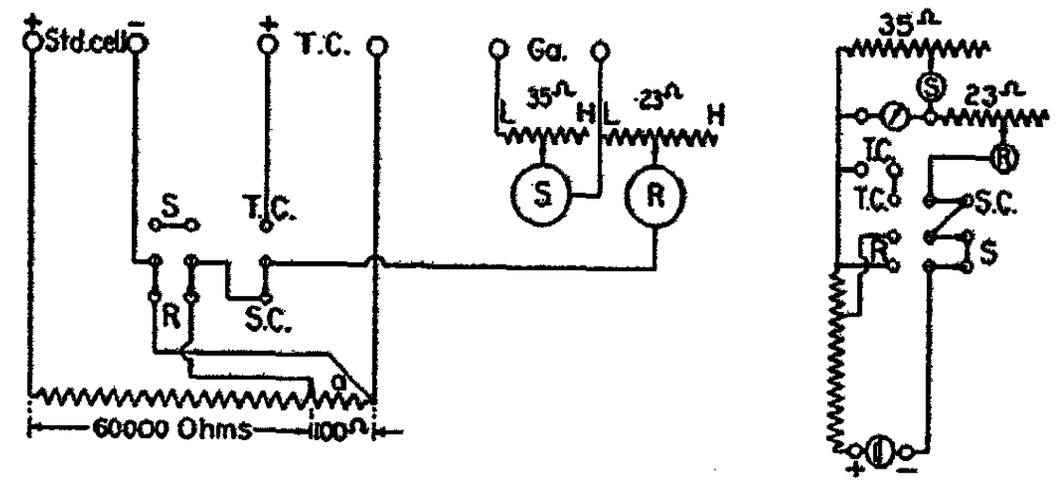

Fig. 8.—Device for Constant Sensibility and Resistance, Thwing Pyrometer.

allows us, by noting the deflections obtained when a Weston standard cell is connected across the galvanometer and adjusting device, to make sure that the galvanometer has not changed from the conditions under which it was calculated,

or if it has changed, to restore it to the original conditions by varying the resistances.

The first couple was in the usual long 1″ tube, but showed grave faults in the matter of prompt return to zero, the couple having too great heat capacity. The next one was similarly mounted, but its return to zero was not good, and placing the hand on the tube just over the couple would heat the cold junction and give a large negative reading. Blowing on the tube at that point would cool the cold junction and increase the deflection by an amount corresponding to a few hundred of degrees increase in the temperature of our hot body. Hence it was necessary to insulate the couple from outside influences, and to this end it was placed in a large wooden box. To prevent heat reaching the cold junction by conduction along the metal tube, the diaphragms were of sheet aluminum held between steel rods fastened to the outside of the wooden box.

This solved the problem of insulating the couple from outside influences, but the steel rods were so flexible that every time the instrument was moved the relative positions of the diaphragms, and hence their effective size, was changed, and no concordant results could be obtained.

Next the diaphragms were held by a stiff brass framework, which solved this last difficulty. The instrument in its present form consists of the usual tiny couple at the back of the aluminum cone, contained in a wooden box, of half-inch stuff, whose outside dimensions are $11^1/_2'' \times 11^1/_2'' \times 15^1/_2''$ long. The cone is 6″ from the front wall of the box. A $^1/_2''$ diaphragm is placed 20″ from the box, and an iris diaphragm, arranged with projecting pins acting as stops so as to give two definite sized diaphragms ($^1/_4''$ and $^5/_{16}''$) without any uncertainty of setting the pointer on a given mark, at $3^1/_2''$ away. In order to allow removing the instrument and replacing it in the same place, its three legs (of adjustable height) fit into depressions in three brass plates, each bearing sharp points on the bottom by which they are stuck in the wood of the table on which the instrument is placed. A dust-proof cap

fits over the opening in front of the cone when the instrument is not in use.

The pyrometer is centered by noting the position of the spot of light on the diaphragms, and moving the box till they are in the center of the spot. Using the $^5/_{16}$" diaphragm, the instrument can be placed 18" to 20" from a hot body 1" in diameter without exceeding the limits of the field. With the $^1/_4$" diaphragm, this distance from the hot body may be considerably increased.

The instrument was calibrated against the spectrophotometer and the Wanner, since Dr. Thwing had no facilities for calibration at such high temperatures. The data are plotted in Fig. 9, showing scale deflections against temperatures.

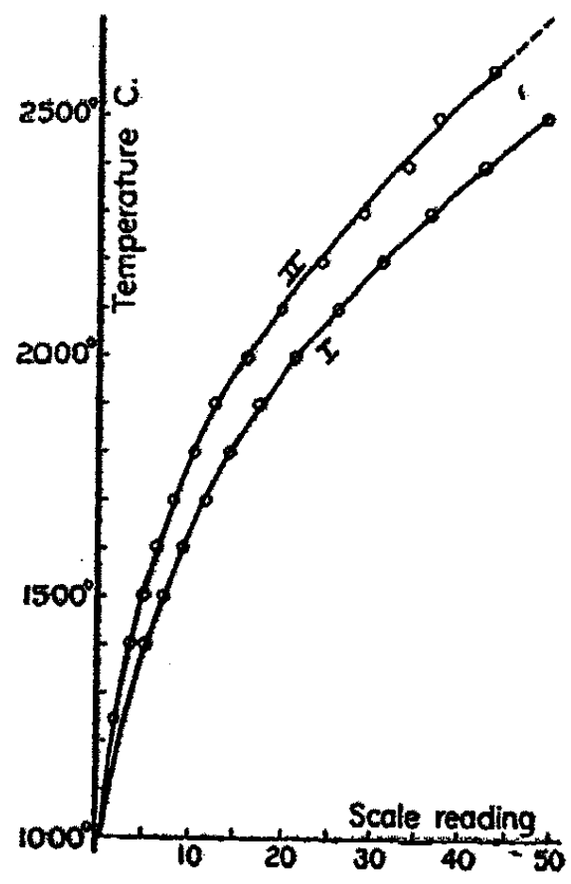

Fig. 9.—Calibration Curves. Thwing Pyrometer. Curve I, with $^1/_{16}$" diaphragm. Curve II with $^1/_4$" diaphragm.

From Figs. 6, 7, and 9 the relative sensitiveness of the Wanner, Morse and Thwing instruments can be found for any temperature, since the Wanner may be set to about half a scale division, the Morse filament may be matched to about two

milliamperes, and the Thwing readings may be made to a fiftieth of a centimeter on the 50 cm scale, and may be reproduced to at least a tenth of a centimeter. At the highest temperatures the Thwing is the most sensitive of the three.

Radiation pyrometers, like the Féry and Thwing, should follow the Stefan-Boltzmann law, $E = K (T^4 - T_o^4)$ or $E = \sigma T^4$ when $T_o = 0$. Here E is the energy of total radiation visible and invisible, T the absolute temperature of the hot body, T_o that of the pyrometer, and K and σ, constants. (Waidner and Burgess [44, p. 474]). When the radiation E falls on the "hot" junction of the tiny thermocouple of the Thwing instrument, it is transformed into heat, which produces an e.m.f. in the couple. If, then, the e.m.f. temperature relation of the couple is a straight line function, and if the galvanometer has a straight line function between e.m.f. and scale deflections, then the relation between galvanometer deflections and the fourth power of the absolute temperature of the radiating source should be a straight line function. On plotting the data shown in Fig. 9 in this way, however, a slight curvature was found.

In order to determine if this was due to deviation from black body radiation of the temperature tube, or to deviation from a straight line relation in the couple or galvanometer, we tried to determine the e.m.f. scale deflection curve for the galvanometer, with its compensating device in series with it, using a Weston potentiometer. The contacts on the tenths of ohms dial had apparently become dirty, so that direct measurement on the galvanometer as it stood, using only the tiny e.m.f. equivalent to that generated by the couple, was impossible. This e.m.f. is of the order of 0.00005 volts per scale division (one centimeter) of the galvanometer. 100,000 ohms was put in series with the galvanometer and adjusting device; then varying the e.m.f. by using the 1,000–15,000 ohm dial, so that slight differences in contact resistance due to dirt became negligible, it was found that the e.m.f. scale deflection curve was an exactly straight line. This indicated that the discrepancy was due to a deviation of the

e.m.f. temperature relation of the couple from a straight line.

To test this, Dr. Thwing loaned us another couple, said to be a duplicate of the one in our pyrometer. The couple was connected to the galvanometer plus its compensating device, the cold junction being kept in melting ice, and the "hot" junction in a beaker of water. Delicate Beckmann thermometers that could easily be read to $^1/_{100}$ degree were fastened to the hot and cold junctions by rubber bands. The temperature of the hot junction was varied by changing the temperature of the water in the beaker. Readings were taken over the whole scale and a slight curvature found in the temperature-scale deflection curve. This gives us a correction for the curvature of the temperature-e.m.f. relation of the couple, plus any deviation in the e.m.f. scale deflection curve of the galvanometer, though from the results with the potentiometer it is doubtful if any such deviation exists.

We found that the difference in temperature of the hot and cold junctions to give a deflection of 50 scale divisions on the galvanometer was only 5.15° C, and to give 38.5 only about 4°. By reference to Fig. 9, it will be seen that with the larger diaphragm a temperature of 2500° C at the hot body only causes a rise in temperature of 5.15° at the hot junction of the couple, or of only 4° with the small diaphragm. This explains why in the metal tube form of the Thwing the couple was so very sensitive to outside influences. As a consequence of the information gained in working with the special instrument, Dr. Thwing is now putting out his commercial couple with a wooden cylinder 10″ long and 3″ in diameter, about the couple. We tested out such a couple and found it to be perfectly protected by the wooden box. While most of his commercial instruments do not use so delicate a couple as this special one, yet the addition of the wooden cylinder must make the commercial instrument vastly more reliable.

Correcting the scale deflection readings back to equal

temperature increments at the hot junction of the tiny couple, and plotting against the fourth power of the absolute temperature of the hot body, we get the curves in Fig. 10, which are seen to be straight lines.

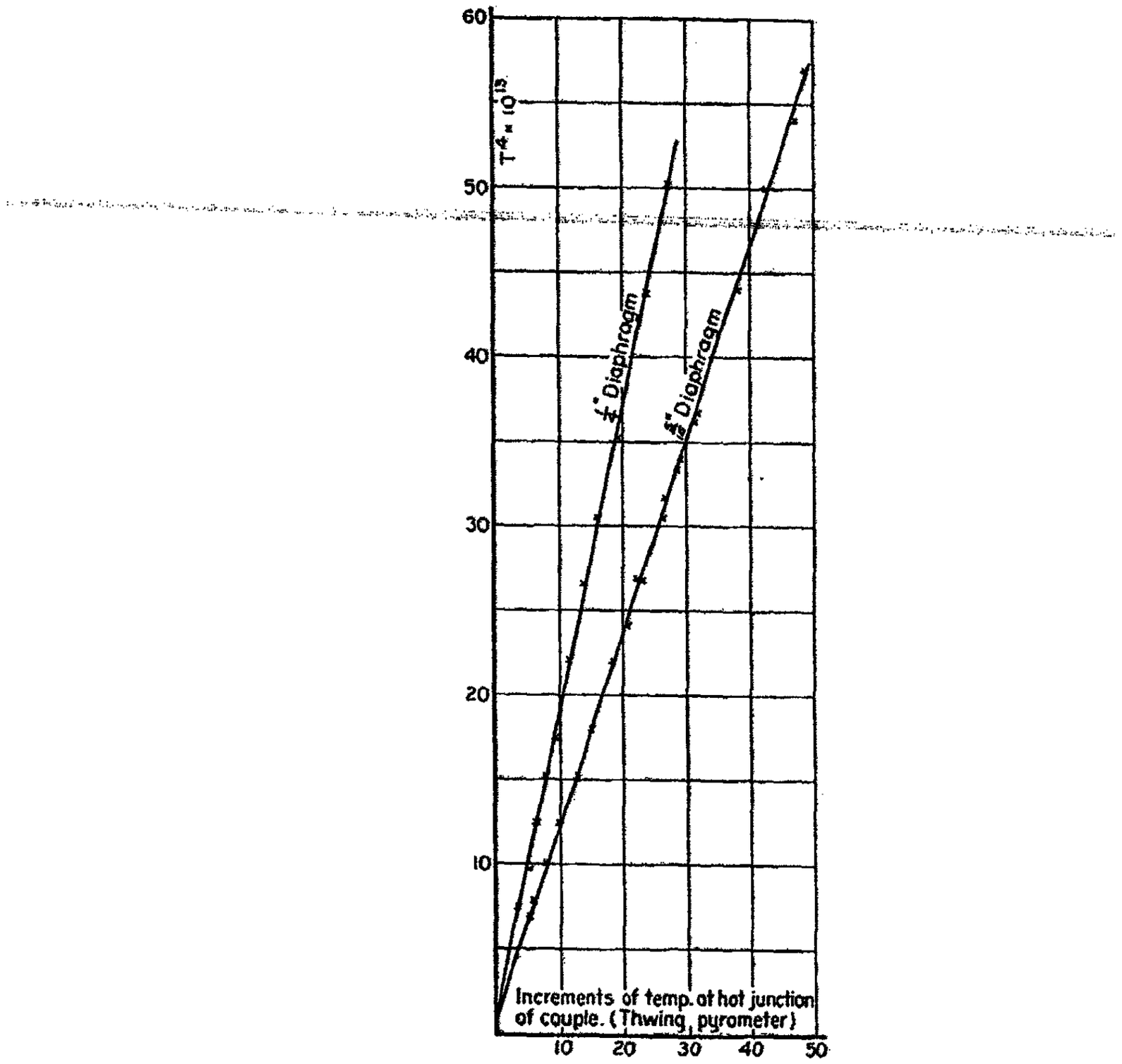

Fig. 10.—Stefan-Boltzmann Law Curve.

The agreement between the Stefan-Boltzmann law used by the Thwing, and the Wien law used by the spectrophotom-

eter and the Wanner, is complete and shows that our temperature tube is giving sensibly complete radiation, not only for optical pyrometers using red light, but also for total radiation instruments. Waidner and Burgess [44, p. 256] have found the Wien and Stefan-Boltzmann laws in accord at 3570° absolute, the temperature of the arc, and Lummer and Pringsheim[26] found them to agree at 2300° absolute.

Now we have all three pyrometers calibrated to read over the 1700°–2500° range we are interested in. It is more or less of a toss-up which pyrometer is the best for our purposes. The Wanner has been available longer than the other instruments, and through long use we have become accustomed to it, and place considerable reliance in it. It, however, requires constant checking against the standard amyl acetate lamp, which is a nerve-racking job, owing to the inconstancy of the light due to flicker from the tiniest draught of air, or the breath of the observer. A black body in a platinum or nichrome furnace, with its tempeature read by a standard thermocouple is a much better means for checking the normal number of the Wanner.

The Morse instrument has to be calibrated empirically, and there is always the danger of deterioration of the lamp. With a properly aged lamp this is slight and may always be checked by the black body as above. Though at present we rather prefer the Wanner to the Morse for this particular problem, our attitude might be reversed had we used the Morse as much as the Wanner, particularly in view of the great advantages of the small field required by the Morse.

The Thwing, in the special box form, is unwieldy if it has to be moved from one temperature tube to another. Its sensitiveness is the best of the three above 1800°, and for use with a single temperature tube, where it can be left in position throughout an entire run, it is ideal. There is no question of inaccuracy of watching a field due to fatigue of the eye, as in the other two. It is likely that for most of the further work on the carborundum furnace it is planned to

undertake in this laboratory, the Thwing will be the most satisfactory of the three.

Any one of the three, then, properly calibrated, will serve to measure the temperatures in the carborundum furnace.

Now, having studied the variables affecting the temperature tube, and calibrated our thermometers, we may proceed with our original object, the measurement of the temperatures in the carborundum furnace.

The values given in the literature for the formation and decomposition temperatures of crystallized carborundum and of siloxicon, vary greatly. Acheson[76] gives 3500°–4000° F as the range over which siloxicon is formed. Dunlap[76] gives 7000° F as the formation temperature of carborundum, and 4500°–5000° F as the siloxicon range. Wright (2, p 41) gives the same figures. Scott[77] says that siloxicon goes over into carborundum at 3000° C. Kunz[78] gives Moissan's figures[11] of 1200°–1400° C as the temperature at which SiC is formed in fused silicon (not in the regular furnace) and 3400° C as the temperature of decomposition of SiC. Thompson[79] speaks of the formation of SiC by melting Si in a graphite crucible at "ordinary heats." Pring,[80] working at extremely low pressures, gives the formation temperatures of SiC from Si and C as 1250°–1300° C and says the reaction goes on rapidly above 1400°. He finds that in practically a vacuum, Si containing 5 percent Fe and 0.7 percent Al reacts with carbon at all temperatures above 1200°, the product being crystalline under the microscope and hence SiC and not siloxicon. Greenwood[81] finds that at pressures of 2 to 3 mm Hg, carbon reduces silica at 1460° C, forming either SiC or siloxicon. Pring and Fielding[82] find that at very low pressures carbon interacts with Si from the vapor of $SiCl_4$ mixed with an excess of H_2, to form SiC at 1700° C. With the addition of C_6H_6 vapor the reaction goes at 1700–1850°. The Dictionary of Chemical and Metallurgical Material[83] gives 2250° C as the decomposition point of SiC. Stansfield (5, p. 152) says "The temperature of the carbo-

rundum furnace has never been measured, and has been supposed to be as high as 3000° C." Stansfield quotes Tucker and Lampen[84] giving the dissociation temperature of SiC as 2220° C. He further says (5, p. 56) "Siloxicon has been said to turn into carborundum at 5000° F, or 2760° C, carborundum fire sand to crystallize into carborundum at 7000° F, or 3870° C, and carborundum to be infusible at the same temperature, while it is admitted that these substances are less refractory than carbon, whose boiling point is taken to be 3700° C, or 6700° F. Recent experiments (those of Tucker and Lampen), however, place the formation temperature of carbide of silicon (siloxicon) at 1600° C, its crystallization at 1950° C and its decomposition into graphite and silicon vapor at 2220° C."

This work by Tucker and Lampen has brought some order out of chaos, and gives the only figures we can put any sort of reliance in as showing the actual temperatures in the commercial furnace, using the commercial charge, and working at atmospheric pressure. Lampen[85] gives the following: formation of siloxicon about 1615° C; decomposition of siloxicon and formation of crystalline carborundum between 1900° and 2000°; decomposition of SiC to graphite, 2220° to 2240°.

Tucker and Lampen[84] placed a graphite tube transversely through a carborundum furnace, determined the temperature gradient through the tube by means of a Wanner pyrometer sighted on a movable plug, much as we did in getting the gradient through the different kinds of tubes, then when the run was over, cut down through the furnace and measured the width of the graphite, carborundum and siloxicon zones. They found 2218° and 2223° C for the temperature of the point in the tube at the same distance from the center of the furnace as that at which SiC was decomposed to graphite in the charge; and 1980° and 1920° for the temperature of the point corresponding to the formation of SiC in the charge. They do not fix a figure for the formation temperature of siloxicon, but from their curve it seems to be about 1600°.

The chief criticism here is the tacit assumption that the temperature gradient through the graphite tube is the same as that through the furnace. Our determinations of the gradients in the carbon, graphite and carborundum tubes, and in the furnace itself, show that this is not the case. Throughout the graphite zone the tube and furnace gradients will be practically the same, hence we may expect the value 2220° for the decomposition temperature to be about right. The temperature at the junction of the carborundum and siloxicon zones, however, may be expected to be really considerably lower than that shown in the graphite tube, owing to the higher heat conductivity of the graphite. Moreover, there is a discrepancy of 60° between their two determinations, 1920° and 1980°.

In our preliminary work, using the elbow form of temperature tube, made of carbon, not correcting for the difference in temperature between the two surfaces of the plug, and reading temperatures with the Wanner without any glass, or with the thick dark glass supplied with the instrument, we get the following results:

Run 50	Crystallized SiC at 1790°–1805°
Run 52	Crystallized SiC at 1820°. Crystallized SiC formed $1^1/_4$″ away from the core, which only reached 1950°.
Run 54	Much siloxicon at 1625° and below—no SiC
Run 55	Crystallized SiC 1″ away from the core which reached 1920°
Run 56	Crystallized SiC at 1820°
Run 57	Crystallized SiC below 1850°, formed 1″ from core, which reached 1910°
Run 58	Crystallized SiC at 1825° to 1850°
Run 59	Crystallized SiC at 1800°—much at 1825°—none at 1790°
Run 60	Crystallized SiC at 1800°–1825°—also below 1850° in another tube

In these preliminary experiments we were limited as to power, and seldom reached the dcomposition temperature of SiC, so we had no data on that point. These readings are not accurate to more than 25°, and since no corrections were made, the total inaccuracy may be 50°, but they do

show that the 1950° figure for the formation of SiC given by Tucker, is too high.

This seems reasonable, too, when we consider that in the commercial furnace they get, from the core out, first one to two inches of graphite, then ten to twelve inches of crystalline SiC, then two to four inches of "fire sand" or siloxicon, and then about two inches of unchanged charge. Tucker's figures—2220° to 1950°—give only 270° for the range over which crystalline SiC is formed in the furnace, and this seems a small temperature drop for a whole foot.

After we had evolved the fumeless tube, and calibrated the pyrometers, we made further measurements to settle this point on a furnace of the size and shape shown in Fig. 1, filled with 150 lbs. of the normal charge. In this were placed, side by side, two carborundum tubes of the dimensions given below, Fig. 2, the center line of each being 2″ from the middle of the furnace, *i. e.*, they were placed symmetrically, with their centers 4″ apart. One of them had the back of its plug $^3/_4$″ from the core, and the other had it 1″ from the core. The temperature was raised, at first fairly rapidly, and then less so, till at the end of the $2^1/_4$ hour run, the last 50° took 20 minutes and the last 20° took ten minutes. We will call this Run A. The same thing was done in the same way in other furnaces in Runs B and C, save that in B the tubes were respectively $^1/_4$″ and $^1/_2$″ back from the core, and in C, respectively $2^3/_4$″ and 3″.

Table XVIII shows the results. The temperatures given are the highest temperatures reached in the respective runs:

TABLE XVIII

Run	Tube nearer the core				Tube farther from the core			
	By Wanner	By Morse	By Thwing	Average	By Wanner	By Morse	By Thwing	Average
A	1820	1823	1825	1822	1790	1800	1800	1797
B	2240	2230	2230	2233	2190	2180	2180	2183
C	1547	1550	....	1548	1526	1520	....	1523

By reference to Table VII we see that at 1800° the correction for drop through the $^3/_{16}$" plug is +25°, at 2200° +17°, and at 1550° +31°. The rate of heating employed here was very comparable to that used in determining these corrections, so they apply without change.

This gives us the following corrected values:

TABLE XIX

Run	Nearer tube	Farther tube
A	1847°	1822°
B	2240	2210
C	1579	1554

Now as to results. In Run A we found crystalline SiC past the end of the nearer tube, and just to the farther one. There was a solid wall of SiC back of the nearer plug when it was pulled out, and there were many crystalline specks clinging to the back of the plug.

In Run B, the nearer tube had graphite on it $^1/_8$" past the end, while the farther tube was about $^1/_8$" outside the graphite zone. In Run C there was siloxicon $^1/_4$" past the end of the nearer tube and about $^1/_8$" past the ends of the farther, that is, even the farther one was a trifle above the formation temperature of siloxicon.

These give us our final figures; decomposition point of SiC, 2220° ±20°; formation of crystallized SiC, 1820 ±20°; formation of siloxicon, 1540° ±30°. The ±30° allotted to the siloxicon is greater than the ±20° given to the others, because of the greater difficulty of telling just where the zone begins.

This value for the graphite point is checked by the run tabulated in Table IV, where the highest temperature reached was 2220° and where graphite had just begun to be formed. This agrees exactly with Tucker's figure. Our figures, however, are 130° lower for the carborundum point, and 60° lower for the siloxicon point.

Tucker used about 18 lbs. of charge against the 150 lbs. used in our furnace. His movable plug was $^3/_8$" thick and its exact position during readings is not stated, so we cannot

tell whether or not there is any error due to disregard of temperature drop through the plug. Tucker's graphite tube was 1" O.D. and $^3/_4$" I.D. somewhat smaller than our temperature tube. If we assume, however, that conditions in his tube and furnace were comparable to those in our larger furnace and tube, we can get an approximate correction for the error introduced by his disregard of the difference between the temperature gradient of tube and furnace, by using the data obtained in our work on the gradients through graphite and carborundum tubes, Tables IV and V.

Tucker has fortunately given us his actual readings. Changing his distances into inches, measured from the edge of the core, instead of centimeters measured from the center, so as to correspond with ours, and averaging his figures for both sides of the furnace, we get the following:

TABLE XX

Material	Distance from core						
	0"	$^1/_2$"	1"	$1^1/_2$"	2"	$2^1/_2$"	3"
Our graphite tube	2000°	....	1885°	....	1730°	....	1580°
Our SiC tube	2000	....	1860	....	1630	....	1515
Tucker's graphite tube	2240	2130°	2060	1980°	1900	1810°	1750
Our SiC tube	2220	2100	2005	1930	1830	1755	1660

These are plotted in Fig. 11.

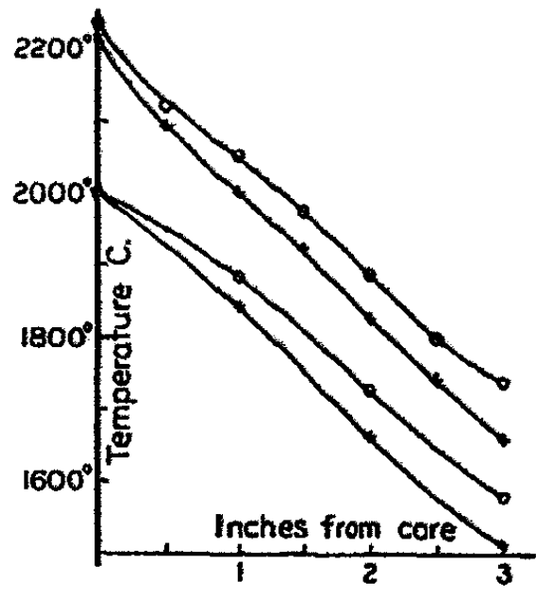

Fig. 11.—Tube Temperature Gradients. Circles denote graphite tubes. Crosses denote carborundum tubes.

Tucker found SiC on one side of the core at 1940° and at 1900° on the other side. This core temperature was 20° higher than ours, but the conditions are at least roughly comparable.

1940° in the graphite tube corresponds to 1870° in the SiC tube, or in the furnace, and 1900° corresponds to 1830°. Hence his lower figures, thus corrected, comes within the 1820° ±20° indicated by our determinations.

If we continued these curves down to the siloxicon point, given by Tucker as 1600° and by us 1540° ±30°, Tucker's corrected value would give about 1500° for siloxicon. However, on reading his paper it will be noted that Tucker does not appear to base his 1600° value on the run in the furnace with the movable plug method, but rather on the work of Lampen, who mixed sand and coke in a tiny graphite boat heated inside the tube resistor of a tube furnace, and determined the temperature by sighting on the graphite boat with a Wanner. In this way he finds about 1600° for the siloxicon point, 1900° and 2000° C for the SiC, and 2220° for the graphite point. Since these determinations differ by 100° at the SiC formation temperature, it is plain that they cannot lay claim to any great degree of accuracy.

Hence from our accumulated evidence and from the very fair agreement with Tucker's corrected results, we believe the figures 1540° ±30° for the formation of siloxicon, 1820° ±20° for that of crystallized SiC and 2220° ±20° for the decomposition of SiC, to be correct within the limits given.

We have not attempted to fix a temperature for the formation of "Amorphous SiC" which is often stated to occur between the zones of crystalline SiC and of siloxicon, since we consider that it is at least an open question whether any such substance exists, or at least, whether it is formed either in commercial or laboratory furnaces. Direct determination of the question by analysis of the zone next to the crystalline SiC is impossible with the product made in a laboratory scale furnace. The siloxicon grades off from a whitish gray on

the outside to a dark greenish gray inside. There is no line of demarcation nor any physical property by which "amorphous SiC" may be distinguished from siloxicon. As soon as we get beyond the point where the change in color of the siloxicon ceases to be continuous, microscopic examination shows the presence of crystalline SiC mixed with the amorphous siloxicon. We asked Mr. Tone, of the Carborundum Co., if he could give us for analysis samples of "amorphous SiC" from the commercial furnaces, where the zones are wider. He said that if a zone of amorphous SiC does exist, he does not know where it begins or ends, and cannot separate it.

Tone[86] very properly sidesteps the whole matter by calling the zone extending from crystallized SiC out to unchanged charge, "carborundum fire-sand." FitzGerald[87] says that Schützenberger obtained amorphous SiC by heating SiC and carbon in a gas-fired furnace provided with blast. The formation of regular carborundum in this way has been reported by Thompson.[79] Schützenberger's original article,[88] however, only says it was pulverulent. He gives no microscopic examination on which to base the belief that it was really amorphous. Moreover, Moissan got crystals by this method. FitzGerald says that outside the SiC zone is a small zone of grayish green "white stuff" considered to be amorphous silicon carbide—outside this being unchanged charge. He does not use the term siloxicon, or oxy-carbide, at all in this paper.

The statements of Mulhauser[89] in 1893 that he obtained amorphous SiC have gone down through the literature and form the chief basis of the belief in that material. He took the zone just outside the crystallized SiC, pulverized, floated, ignited, boiled with HCl, extracted with water, dried, and treated with HF and H_2SO_4. After *long treatment* with HF and H_2SO_4 he fumed off the H_2SO_4 extracted with water, dried and analyzed, obtaining

C	29.73 percent
Si	65.42
$Fe_2O_3 + Al_2O_3$	5.09
CaO	0.38
MgO	0.21
	98.93

He started with 100 parts of coke containing 90.24 percent C, 100 parts sand containing 99.55 percent SiO, and 25 parts NaCl. Now this is a large excess of carbon, in which case there does not seem much justification in figuring Fe and Ca, at least, to the oxides. Even taking his figures just as they stand, there is one percent that may be oxygen.

The above was taken from his German article. In his paper in English he says he purified and crystallized SiC by an HF treatment, and in the treatment of the "amorphous carbide of silicon," "as it was evident that it was an amorphous form of SiC," a similar process of purification was used.

Now it is well known, as Potter states,[90] that siloxicon is attacked by HF with elimination of Si and O, leaving a residue which after ignition approximates the formula SiC. Hence Mulhauser's method of analysis was exactly such as to prevent him from finding out that his amorphous material from the furnace really was siloxicon. In the English paper Mulhauser states that the zone just outside the "amorphous carborundum" is unchanged charge. In the German article he analyzes the zone just outside the amorphous zone, and finds $AlSi_2O_7$, though the formula staggers him a bit and he concedes that the question of the composition of this zone is open.

The composition of siloxicon is given as varying from Si_2C_2O to Si_7C_7O, and while most authorities say it is "about" Si_2C_2O, almost all agree that its composition is very variable. It is seldom looked upon as a true chemical compound.

To illustrate the loose way in which the terms "siloxicon" and "amorphous carborundum" are used, we quote from Tone,[91] "In any mixture of carbon and silica the

first products to be formed when the charge is heated to the temperature at which silica begins to reduce, are silicon-oxygen-carbon compounds in which these elements may be combined in various and most complex proportions, the compounds being at the same time intimately associated with free carbon and free silica. Typical of these silico-carbides are siloxicon and amorphous carborundum." Also the following from Potter [90, p. 209].

SPECIFIC HEAT DETERMINATIONS

No.	Substance	Sp. heat	Remarks
30	SiC *amorp.*	0.1894	Average of 4 detns. made from siloxicon
32	Siloxicon	0.1911	

We admit that an amorphous material corresponding fairly well with the formula SiC may be obtained by long treatment of siloxicon with HF, and ignition, but we doubt very much if any such substance is obtained directly in the carborundum furnace. Our own idea of the matter is that the siloxicon zone consists of a complex series of solid solutions of Si, C, and O, the proportion of O being greater at the outside of the zone and lower at the inside, corresponding to the gradation of color from light to dark gray-green, though this is of course merely an hypothesis. At any rate, we feel justified in disregarding the so-called zone of amorphous carborundum in our temperature determinations.

During the course of this temperature work, a couple of observations were made which may be of enough interest to record. With the furnace and core as given in Fig. 1, using the normal charge, it was found very difficult to get the temperatures above about 2400°. In some cases we have reached as high as 2675° C, read by the Wanner, but these higher temperatures were reached in a furnace packed tightly with crushed carborundum instead of the regular charge, using a core of small original cross section, and heating the furnace up at a rapid rate. In ordinary cases, 2400° was the high mark.

This was not due to reaching the limit of power that the generator would supply, since the kw would increase, while the temperature fell. In one run where the furnace was taking about 32 kw and giving 2300°, the power rose to 35 kw and over, while the temperature dropped slightly below 2300°.

The reason is not far to seek. As soon as we get above 2220° the SiC that has been formed decomposes into graphite, which then forms part of the resistor. The cross section of our effective core is thus increasing at so great a rate that even with increased power the calories per unit of effective core surface are less than formerly, and the temperature drops promptly. This would not be the case if graphite happened to have its regular heat conductivity without its electrical conductivity. Consider the data in Table XXI:

TABLE XXI

Time	Volts	Amps.	K.W.	A Temp. at core	B Temp. 2″ back	C Temp. 2½″ back	D Temp. 4″ back
8.10	160	25	4.0	20°	20°	20°	20°
8.20	150	50	7.5	....	....	....	....
8.30	155[1]	50	7.7	965	....	....	30
8.40	155	100	15.5	1190	....	....	60
8.50	98	250	24.5	1725	....	....	80
9.00	90	280	25.2	1990	....	....	160
9.10	73	325	23.7	2140	1000	850	520
9.20	67	360	24.1	2200	1181	1055	940
9.30	74[1]	450	33.3	2280	1410	1190	1080
9.40	93	540	39.4	2300	1665	1380	1250
9.50	70	590	41.3	2330	1830	1430	1350
10.00	70	600	42.0	2360	2080	1830	1520
10.05	62[2]	550	34.1	2330	2120	1830	....[3]
10.10	46[2]	400	18.4	2300	2020	1830	....
10.15	30[2]	100	3.0	2250	1930	1770	....

In this run three temperature tubes were used, A, at the core; B, 2″ back; and C, 2½″ back from the core. A thermo-

[1] Power increased by means of field rheostat.
[2] Power decreased by means of field rheostat.
[3] Couple removed.

couple, D, in a porcelain tube with the end ground off to a thickness of 0.4 mm, was placed 4″ away from the core. The temperatures given are not corrected for drop in temperature through the plug.

In Fig. 12 we have plotted some of the data of Table

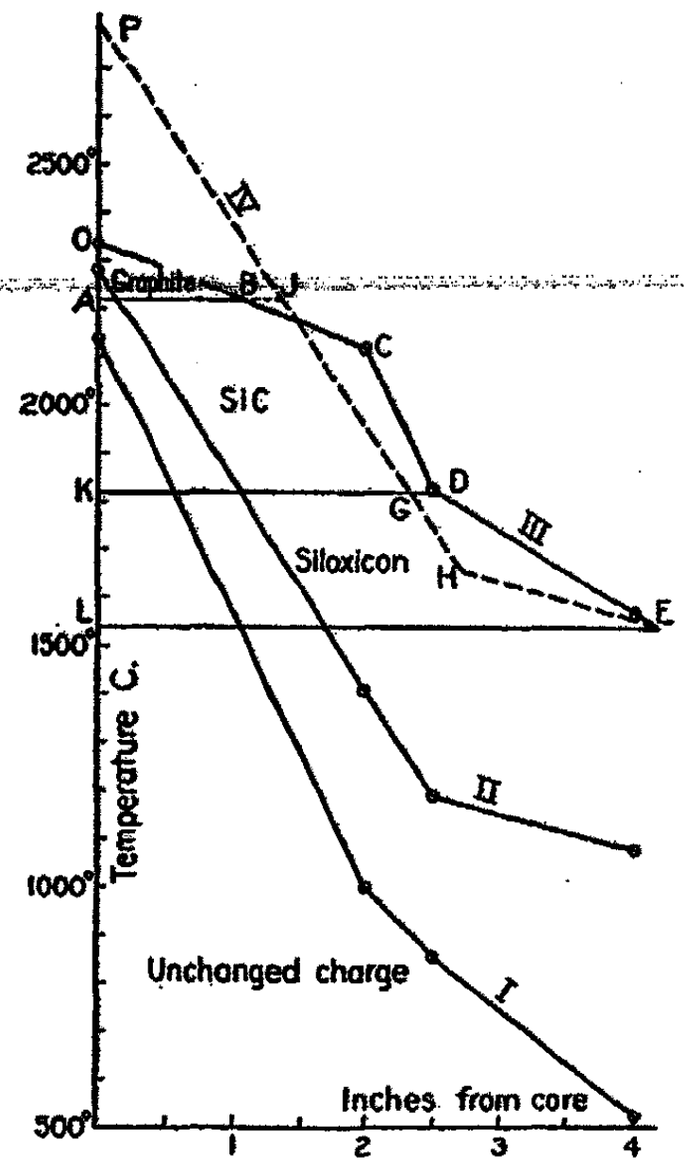

Fig. 12.—Furnace Temperature Gradients.

XXI. Curve I is the temperature gradient after the furnace has been running 1 hour, Curve II that after 1½ hours, and Curve III that corresponding to the highest temperatures reached. As will be seen from the table, we decreased the power just before the normal lowering that would have taken place, due to graphite formation, occurred, because we wished to keep the temperature at tube C from rising above 1850° (corrected), in order to get a determination of the formation

temperature of SiC. Hence the data do not illustrate our point as well as they might. However, the phenomenon of the lowering of temperature was a perfectly general one, and since we seldom had more than two temperature tubes in the furnace during the runs that went up to 2400°, and hence did not determine the gradient so completely as in this run, this case will serve.

In passing we may remark that we found SiC past the end of tube C, about $^1/_8$", and siloxicon about $^1/_4$" past the point where the thermocouple was placed, these observations being in complete accord with our other determinations of the formation temperatures of SiC and of siloxicon.

Inspection of Fig. 12 will show that in any given form of carborundum furnace, at any given rate of heating, there is some maximum temperature above which we cannot go, because the increase in core cross-section will overbalance the power supply. This maximum temperature is far below that which would be attained at the normal stationary state of the furnace for a given power input, if the graphite formed did not carry the current.

For instance, if in Fig. 12 the effective core had remained only 2" thick as at the start, instead of 4" thick at it was at the end of the run, instead of the gradient being in the form of Curve III, it would have been approximately that of Curve II, where we had just reached the temperature of graphite formation, but moved along to some position which we may represent diagrammatically by Curve IV. In the actual case our graphite zone is represented by the area OAB, the SiC area by ABCDK, and the siloxicon by KDEL. In the hypothetical case, our graphite zone would have spread out much farther and the graphite area would be PAJ, the SiC, AJGK, and the siloxicon, KGHEL. The gradient would probably not have exactly the form given, but the change would be in that general direction. Then our SiC zone would be considerably decreased.

In other words, the most efficient carborundum furnace is the one in which the 400° between the formation and de-

composition temperatures of carborundum extends over as long a distance as possible, that is, where we have a flat temperature gradient. The steeper the gradient between 2220° and 1820°, the less efficient the furnace. The auto-increase of the core cross-section keeps the maximum temperature down, and tends to give a flatter gradient. Hence the success of the commercial furnace is largely due to the fact that SiC decomposes into a substance that carries the current and forms part of the resistor.

To this same principle is due the fact that if we wish to get a large yield of siloxicon we must use multiple cores, according to Acheson's patent,[92] since siloxicon decomposes, on heating, into carborundum which is practically a non-conductor of electricity, though a good conductor of heat. The carborundum plays no part in the siloxicon furnace analogous to that of the graphite in the carborundum furnace, hence in the former much more care has to be paid to keeping the core temperature down.

Some data on the gradients through carbon and graphite electrodes was obtained in the preliminary work, and may be worth recording in view of the work now being done by Hering[93, 94], Hansen[95], and Forssell[96] on furnace and electrode design.

Hering[94] gives the following diagram (Fig. 13) for

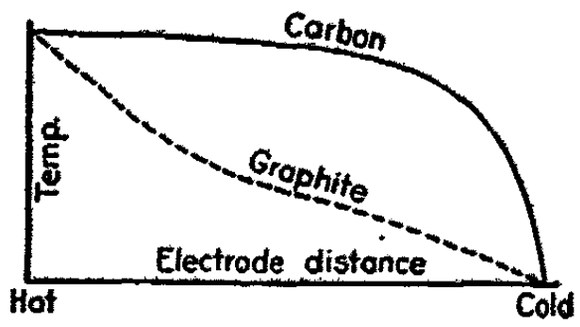

Fig. 13.—Hering's Electrode Temperature Gradients.

the theoretical heat gradients through carbon and graphite electrodes, and concludes from his theoretical considerations that carbon is the worst material for electrodes, on the basis of electrode losses, thus being inferior to graphite. He says,

"Graphite, like iron and unlike carbon, tends to crowd the heat toward the hot end where it belongs."

Our work on graphite and carbon tubes, not carrying current, shows that this is not the case, since at any given point in the tube, for equal temperatures at the hot ends, the graphite is the hotter.

The data given in Tables XXII, XXIII, and XXIV, and plotted in Figs. 14, 15, and 16, show that it is not true for electrodes carrying current, under our conditions. The data were taken in a small furnace where we were limited to the low power at first available, and to poor regulation. The furnace was 24″ long, 14″ wide and 12″ high, inside dimensions, with fire-brick walls, and packed with the normal carborundum charge. The electrodes were cylindrical in shape and 2″ in diameter. They had not been previously used. The core was of 6–12 mesh crushed carbon, 10″ long × 2″ diameter. Just at the junction of the core and electrode a carbon temperature tube of the elbow type was inserted so the plug rested tightly against them both. The temperature of the plug was read by the Wanner pyrometer, no correction being introduced for temperature drop through the plug.

Six inches back from this junction a hole was bored in the electrode to take a porcelain pyrometer tube and thermocouple. At six and twelve inches back from this were bored other holes in which were inserted nitrogen filled thermometers, powdered graphite being packed in the waste space in the hole, so that the thermometer fitted closely. The electrodes rested in a 4″ × 4″, inside dimensions, firebrick trough, filled with siloxicon, the trough extending 2″ past the outer thermometer. They were not water-cooled.

The proper way to take these data would have been to use one carbon and one graphite electrode in the same run, and take readings on both. At that time, however, only one thermocouple was available, so we had to make runs using first graphite and then carbon electrodes. As the power could not be controlled so as to exactly duplicate conditions

in two consecutive runs they are but roughly comparable as to rate of heating and maximum temperature reached.

TABLE XXII

Run 59. New Graphite Electrode

Time in minutes	Volts	Amps.	K.W.	Electrode distances from hot end 0″	6″	12″	18″
				Temperature read by			
				Wanner	Thermo-couple	Thermom-eter	Thermom-eter
0	100	25	2.5	(20°)	(20°)	20°	20°
15	100	52	5.2	850	150	70	40
30	98	97	9.5	1005	280	135	75
45	82	152	12.3	1300	470	235	140
60	73	180	13.1	1600	600	280	180
75	67	193	12.9	1700	700	325	225
90	62	196	12.2	1720	810	385	270
105	60	200	12.0	1730	850	400	295
120	58	200	11.6	1740	905	435	320
135	56	195	10.9	1790	970	460	325
150	56	190	10.6	1860	1020	485	340
165	54	200	10.8	1865	1070	500	345
180	54	190	10.2	1865	1110	515	350

TABLE XXIII

Run 60. New Carbon Electrode

0	100	25	2.5	(23°)	(23°)	23°	23°
15	90	87	7.8	925	60	46	44
30	70	180	12.6	1550	150	100	95
45	65	190	12.4	1830	320	225	210
60	64	200	12.8	1905	470	275	245
75	62	195	12.1	1905	600	290	265
90	60	200	12.0	1945	700	330	275
105	58	195	11.5	1970	815	370	290
120	58	195	11.5	2120	950	400	282
135	57	185	10.5	2120	1090	435	295
150	58	195	11.5	2120	1150	450	300
165	56	190	10.1	2150	1210	470	300
180	56	190	10.1	2180	1270	495	300

TABLE XXIV

Run 61. New Carbon Electrode

Time in minutes	Volts	Amps.	K.W.	Electrode distances from the hot end 0″ 6″ 12″ 18″			
				Temperature read by			
				Wanner	Thermo-couple	Thermom-eter	Thermom-eter
0	100	25	2.5	(24°)	(24°)	24°	24°
15	72	150	10.8	950	125	100	90
30	68	190	13.0	1350	250	180	175
45	66	180	11.9	1450	280	225	220
60	63	185	11.7	1520	425	295	290
75	62	185	11.3	1675	555	310	300
90	60	190	11.4	1770	640	330	315
105	60	170	10.2	1815	755	360	320
120	60	182	10.9	1820	830	370	325
135	59	160	9.4	1900	970	395	330
150	60	160	9.6	1950	1075	405	330
165	60	160	9.6	2000	1185	425	330
180	60	160	9.6	2000	1210	430	330

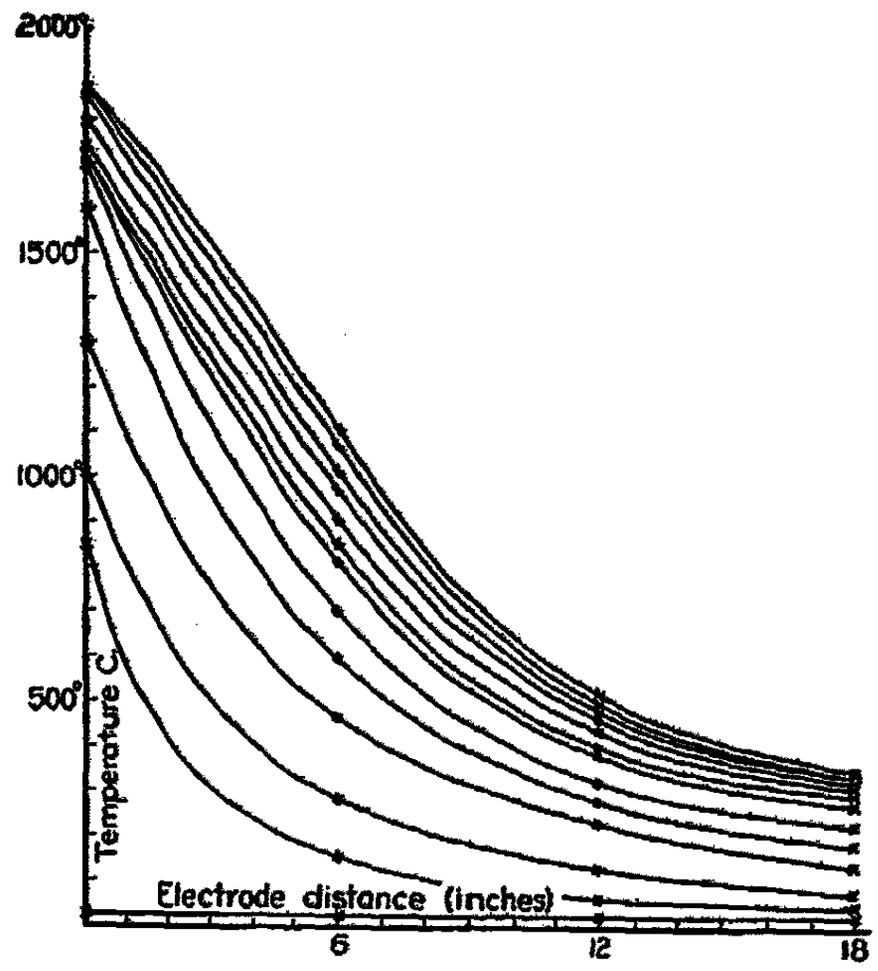

Fig. 14.—Electrode Temperature Gradients—Graphite, Run 59.

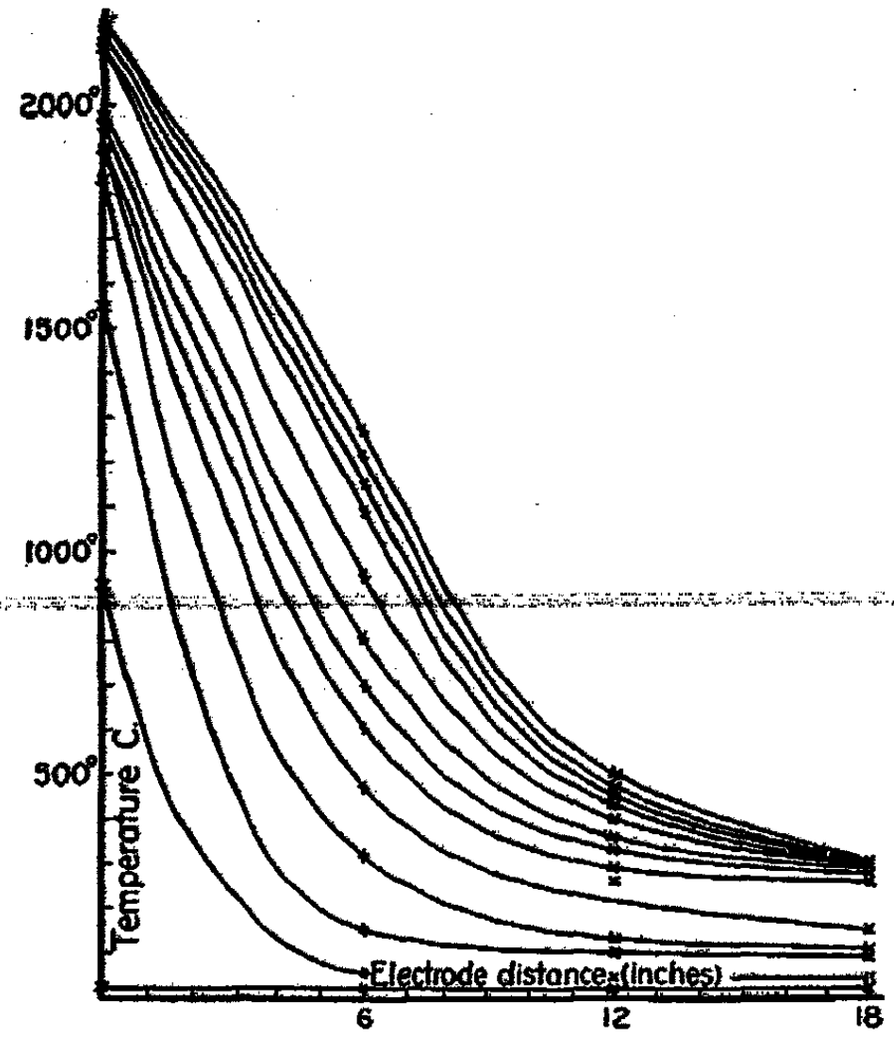

Fig. 15.—Electrode Temperature Gradients—Carbon, Run 60.

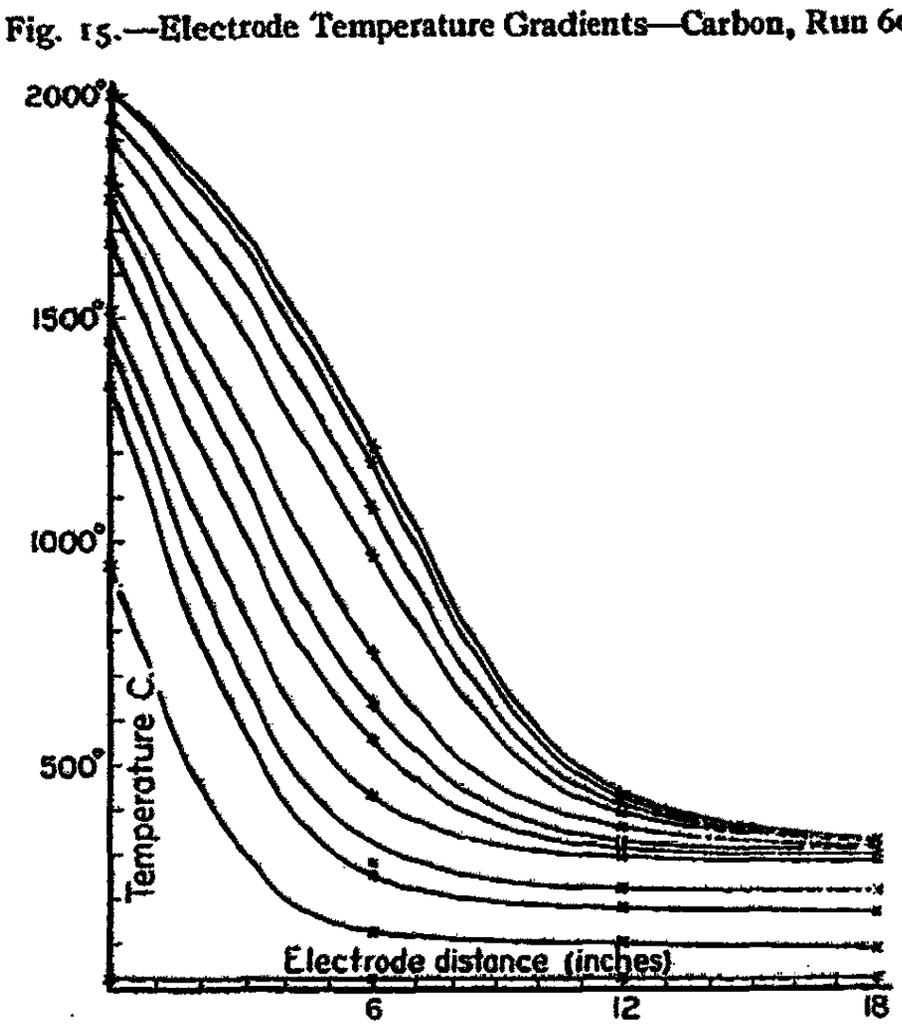

Fig. 16.—Electrode Temperature Gradients—Carbon, Run 61.

Run 61 on the carbon electrode is more comparable with 59 on the graphite than is 60, on account of more nearly equal rate of heating and final temperature. We do not insist on the absolute accuracy of the temperature readings, since there may have been some thermocouple lag and the thermometer may not have fitted tightly enough to give exactly the temperature of the points at which they were placed, but the temperatures cannot be enough out to obscure the results.

These data show that for our conditions, all the factors, as C^2R heating, thermal conductivity lengthwise, and loss of heat from the surface of the electrodes to the packing about them, being taken together, the two materials give temperature gradients that are surprisingly alike. The curves have been drawn diagrammatically through the observed points.

If there is really any such difference in the gradients as Hering's diagram claims, it must be wholly within the first six inches, where we made no measurements. This does not mean that at other terminal temperatures, with other furnace charges and electrode packing, and at other electrode current densities, the gradient will be the same as here given; but for our conditions, the two materials show a marked similarity. This is checked by the fact that no difference in the shape of the football-shaped mass of carborundum and siloxicon that is found after a run, when the unchanged charge is scraped away, has so far been noted whether carbon or graphite electrodes were used, indicating that the electrode losses of the two were not notably different.

Further work on this point by other observers in this laboratory is planned, since by using a tubular electrode with movable plug for temperature measurements, and by noting the rise in temperature of the water passed through the water-cooled electrode holders, the point should be easily settled.

In view of the importance of the work being done on electrode losses and furnace design, it may not be out of place to emphasize that since it is easy to make tubes for tem-

perature observations that are free from fumes, it is perfectly possible to verify experimentally the different theories now in process of evolution. No such theories can be considered of much account till they are experimentally verified. In such experimental work, too great care cannot be taken to have the gradients through furnace and temperature tube the same wherever the movable plug method is used. It is necessary to have them the same with a stationary plug, to be sure of the results, but for the movable plug it is vital if true results are to be obtained.

In the case we have dealt with, the formation temperature of SiC, the error due to disregard of this point was 7 percent at 1800°. Such an error might materially mislead an experimenter seeking the true laws of furnace and electrode design.

Forssell[90] in telling his theoretical assumptions, says that in a furnace containing SiO_2, information may be obtained as to the temperature reached, by noting where graphite, crystalline SiC, and siloxicon are formed on the electrodes, and gives Tucker's values already cited, for these points. In view of this, the present revision of the value for the formation temperature of carborundum should have a distinct bearing on the problem of electrode losses.

Summary

1. The composition of the charge for the carborundum furnace has been studied, and an excess of carbon found advisable.

2. A form of tube for temperature measurement by optical and radiation pyrometers has been devised which minimizes fume troubles.

3. The use of carborundum tubes for the measurement of temperatures in the carborundum furnace, has been introduced, and their mechanical properties studied briefly.

4. The variables affecting the temperature tube have been studied; the cooling effect of the current of air used to suck out fumes, found to be negligible, and the corrections

for the temperature drop through the graphite plug determined.

5. The tube has been found to give practically black body radiation both for optical and radiation pyrometers.

6. The Wanner pyrometer has been made more sensitive over the range desired.

7. The calibration of the Morse thermogage has been examined.

8. A special form of Thwing radiation pyrometer has been installed and improved.

9. All three pyrometers have been calibrated against a spectrophotometer on the basis of Wien's law.

10. Data have been obtained indicating the value 14200 for the constant c_2 in Wien's law.

11. The Wien and Stefan-Boltzmann laws have been found in agreement up to 2500° C.

12. The temperature of formation of siloxicon has been determined as 1540° C ± 30°, that of carborundum as 1820° ± 20°, and the decomposition temperature of carborundum to graphite, as 2220° ± 20°.

13. The discrepancy between the figure ust given for the formation of carborundum and that previously obtained by Tucker has been found to lie in the difference between the temperature gradients of a graphite tube and of the carborundum furnace.

14. It has been shown that "amorphous carborundum" is probably not formed in the commercial furnace.

15. We have discussed the influence of the formation of graphite around the core by the decomposition of carborundum, on the temperatures attained in the furnace.

16. Some data have been given for the heat conductivity of carbon and graphite electrodes.

17. We have emphasized the necessity of having the same temperature gradient through a tube used for optical or radiation pyrometry, as through the furnace.

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a Morse pyrometer and for co-operation in the examination of its calibration, and to Dr. C. B. Thwing for his interest and aid in the improvement of the Thwing pyrometer. Thanks are also due Mr. J. C. Andrews for aid in taking certain spectrophotometric measurements and to Messrs. E. E. Bragg, T. R. Briggs, E. Freudenheim, S. D. Hiltebrant and L. R. Milford, with whom the preliminary observations were made. Above all, hearty thanks are due Prof. Bancroft, at whose suggestion and under whose direction this work has been carried on, for continual kindly advice and encouragement.

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NOTE—Since the above was written, the Reichsanstalt (Henning: Zeit. Instrumentenkunde, 30, 61, Chem. Abstr., 5, 423) has modified the Holborn Kurlbaum form of the Morse pyrometer by adding a collimator.

Cornell University,
March, 1910

NEW BOOKS

Die Absorption. *Gesammelte Abhandlungen über Kolloide und Absorption. By J. M. Van Bemmelen. Mit Unterstützung des Verfassers neu herausgegeben von Wo. Ostwald. 16 × 24 cm; xl + 548 pp. Dresden: Theodor Steinkopff, 1910. Price: paper, 12 marks; bound, 20 marks.*—This volume contains the collected works of van Bemmelen on colloids and absorption. The titles of the fourteen papers are: the nature of colloids and their water contents; the absorbing power of the soil and the absorption compounds formed; the hydrogel of ferric oxide, crystalline hydrated ferric oxide, potassium ferrite and sodium ferrite; the hydrogel and the crystalline hydrate of cupric oxide; the absorption of water by colloids and especially by the silicic acid gel; the formation and structure of gels; absorption; the isotherms of colloidal ferric hydroxide at 15°; the absorption of hydrochloric acid and potassium chloride from aqueous solutions by colloidal stannic oxide; absorption of substances from solutions; action of higher temperatures on the structure of the silicic acid hydrogel; absorption compounds of hydrogels when chemical compounds or solutions may also be formed; the difference between hydrates and hydrogels, and the modification of the hydrogels (zirconic and metazirconic acids); contribution to the knowledge of the properties of hydrogels during desiccation and rehydration.

These papers are fundamental and it is a great assistance to the chemist to have them in a collected and easily accessible form. The advances made by van Bemmelen are really the result of two things: that he made quantitative measurements, and that he realized from the beginning that a gel is not a definite compound. Since the quantitative measurements were necessary in order to prove the second point, it would be possible to condense our statement more and to say that van Bemmelen realized and proved that a gel is not a definite compound. This does not sound like much to-day because the fact is so well known to most of us; but it was van Bemmelen who taught it to us and it was a tremendous step forward when he made it. Even in spite of his work, the beginner in chemistry is still taught that ferric hydroxide is a definite compound.

The chemical world owes thanks to the editor and the publisher for the appearance of this useful volume. *Wilder D. Bancroft*

Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe. *Ein Hand- und Hilfsbuch für die Chemie und Industrie der Kolloide. By The Svedberg. 15 × 23 cm; pp. xii + 512. Dresden: Theodor Steinkopff, 1909. Price: paper, 16 marks; bound, 18 marks.*—The author distinguishes two methods of making colloidal solutions. In the condensation method so called, one starts from a true solution; in the dispersion method one starts from a precipitated material and causes it to go into solution. Under condensation methods we have four subdivisions: reduction; oxidation; hydrolysis; and miscellaneous. Under the dispersion methods we have only two sub-divisions: mechanical and chemical; electrical.

Typical instances of the reduction method are the preparation of colloidal

gold by means of hydrogen, methyl alcohol, or hydroxylamine; Carey Lea's preparation of colloidal silver by means of ferrous sulphate, etc.; Billitzer's method of preparing colloidal gold, silver or mercury electrolytically. The most important instance of an oxidation method is the preparation of colloidal sulphur from hydrogen sulphide. The best known case of hydrolysis is the preparation of colloidal ferric hydroxide. Under miscellaneous methods we have the preparation of colloidal arsenious sulphide in solutions where the concentration of ions is kept low, and the preparation of colloidal silver bromide in presence of gelatine as a protecting colloid.

Typical instances of mechanical or chemical disintegration are found in the peptonizing action of caustic soda on a silicic acid gel or in the alternate action of alkaline and acid solutions on chromium, platinum, iridium, etc. Under the electrical dispersion methods we have the original process of Bredig and the modification of it by Svedberg.

Under each sub-division the author has given a very satisfactory bibliography and the book is an excellent one from every point of view. *Wilder D. Bancroft*

The Relations between Chemical Constitution and Some Physical Properties. *By Samuel Smiles. 13 × 20 cm; pp. xiv + 583. New York and London: Longmans, Green & Co., 1910. Price:* $4.00.—In the preface the author says: "As indicated by the title, this volume does not exhaustively treat of the whole subject in question. For various reasons a few physical properties have been omited from consideration, the more important being Crystalline Form, Optical Rotatory Power, Electric Conductivity, and Heat of Combustion... Some other physical properties, for example, Solubility, Dielectric Constant and Magnetic Susceptibility have been omitted because the relations between them and constitution are not yet sufficiently elucidated to call for special treatment.... A book of this kind runs the risk of satisfying neither the physical chemist nor the structural chemist; but it is necessary to point out that it has been written from the stand-point of organic chemistry. This standpoint has been assumed both from necessity and from personal inclination, the former arising from the fact that by far the greater portion of research in this subject has been focused on the compounds of carbon."

The properties have been classified as mechanical, hermal, optical, and electrical. Under mechanical properties we find capillarity, viscosity, and volume relations. Under thermal properties we have specific heat, fusibility, and boiling point. The optical properties are sub-divided into: refractive and dispersive power; absorption of light; fluorescence; and magnetic rotatory power. Anomalous electric absorpt on is the only electrical property discussed as such.

The book seems to be worthy of the series. For personal reasons, the reviewer has been interested chiefly in the chapters on absorption of light, fluorescence, and anomalous electric absorption; and he confesses to having read these much more carefully than the others. These are probably not the chapters to which most people will turn first. If the others get as much out of the book as the reviewer did, the au hor will have no cause to complain.

Wilder D. Bancroft

The Organic Chemistry of Nitrogen. *By Nevil Vincent Sidgwick. 7¼ × 26 cm; pp. x + 415. Clarendon Press: Oxford, 1910. Price: 14 shillings net.*— In the preface, the author says: "It is becoming generally recognized that organic chemistry cannot be treated satisfactorily without reference to those questions of physical chemistry which it involves. To attempt a separation of the two is to refuse all the assistance which can be derived from what is really the quantitative side of chemistry. The various physical questions are, therefore, discussed as they arise. A full treatment of the phenomena of tautomerism would have required too great an interruption of the main current of thought; but I have tried to indicate the more important points in which they are illustrated by the bodies under consideration. The dynamics of organic reactions is a field which, in spite of the increasing amount recently devoted to it, is still very largely unexplored; and yet it is of the utmost value for elucidating the mechanism of chemical change. I have therefore, made the references to investigations of the velocity of reaction as complete as I could, and the methods of analysis adopted in each case have been described."

The subject is treated under four heads: compounds with no nitrogen directly attached to carbon; bodies containing one nitrogen atom attached to carbon; compounds containing an open chain of two or more nitrogen atoms; ring compounds. As the reviewer has said so often, this is the kind of a book which we want and the more we get of them the better. This particular one is a good specimen of the class and it is difficult to see how any chemist could glance through it without finding something of interest.

On page 25, the author points out that even the determination of the concentration of hydroxyl ions does not necessarily give us the true strength of a base. In an ammoniacal solution, for instance, we have the non-hydrated base NH_3, the undissociated hydrated base NH_4OH, and the dissociated hydrated base NH_4. In the ordinary methods for determining basicity we measure the concentration of the ions in a solution in which the total concentration of the base in all three forms is known, the existence of the first form, the non-hydrated base NH_3 (or R_3N) being neglected. The value of the strength calculated from this is not the true strength but what may be called the apparent strength.

"Hence the apparent strength of the base is smaller than the real strength, and the more so the greater the proportion of anhydrous amine present. When, therefore, the strength of an organic base (other than quaternary) is spoken of, what is meant is the product of two factors, the hydration constant and the dissociation constant. And until recently there was no method known for determining either of these two factors separately. The measurement of the ionization is no use, as the hydration factor comes in to the same extent at every dilution. The determination of the partition-coefficient between water and air or an organic solvent has been suggested; but this does not help us either. The concentration of the R_3N in the other solvent is proportional to that of the R_3N in water, and therefore, also to that of the R_3NHOH: which leaves us where we were before. The problem has at length been solved by Moore. He points out that all methods of solution must fail, in which the observations are all made at the same temperature. If, however, we measure the partition-coefficients and the degree of dissociation at different temperatures, and if we fur-

ther make the assumption, which for small differences of temperature is justifiable, that the temperature coefficients of these two quantities are constant, we obtain a sufficient number of equations to solve the problems. In this way we can determine for any amine (for the method applies equally to all pseudo-acids and pseudo-bases, and to such bodies as carbonic acid and the lactones) the proportion present in the non-hydrated form, and the true dissociation-constant. So far, the necessary data have only been obtained for three substances, piperidine (which does not concern us at present), ammonia, and triethylamine. The results show that in an aqueous solution of ammonia at 20°, about two-thirds is present as non-hydrated NH_3, the rest being mainly NH_4OH and a small quantity of ions; in the case of triethylamine only about a third is in the anhydrous form, as $(C_2H_5)_3N$. From these data the true dissociation constants of these two bases can be calculated and are found to be at 20°:

Ammonia $K = 5.23 \times 10^{-5}$

Triethylamine 64×10^{-5}.

That is to say, the introduction of three ethyl groups into ammonia has increased the constants only twelve-fold. We should, therefore, expect that the introduction of a fourth ethyl group, in tetraethyl-ammonium hydroxide, would involve a further increase only to about 150×10^{-5}, which would mean that it was still a very weak base. But as a fact, the quaternary hydroxide is an excessively strong base, comparable to potash, for which K is too high to be measured and is certainly greater than one. It therefore appears that the first three ethyl groups produce only a small increase in the basicity of ammonium hydrate, while that produced by the fourth is enormous. It has long been known that the quaternary bases were far stronger than the others, but until the true dissociation constants had been determined it was possible that this might be due to the unknown quantity of anhydrous base present in the latter cases but not in the former. This is no longer possible; and the sudden increase in the quaternary bases certainly seems to point to a difference between their constitution and that of the hydroxides of the primary, secondary, and tertiary amines. If we are not prepared to accept a formula such as Werner's, there are two possible explanations. One is that the data on which these calculations are based (especially those for triethylamine) may be incorrect. But even if they are to be accepted, and this sudden change of basicity really occurs, it can be explained on the assumption of analogous structures for the tertiary and quaternary hydroxides, and without having recourse to any new theories of valency. If we say that the five valencies of pentavalent nitrogen are all equal, this only means that the relation between any five groups and the nitrogen atom is determined by those groups themselves, so that (excluding stereoisomerism) isomeric arrangements are impossible. It is nevertheless quite conceivable, and indeed probable, that three of the nitrogen valencies (those of trivalent nitrogen) are essentially different from the other two; and that when successive alkyl groups are introduced into ammonium hydrate they fill up these three places first. If so, the introduction of a fourth group, which must now take up one of the other two positions, may be expected to produce an effect on the molecule different from that produced by any of the other three."

On p. 73 we find an interesting discussion of the diimines.

"The absence of color in these compounds is important, in view of their

undoubted quinoid structure. It is commonly assumed that all quinoid compounds are colored, like the quinones themselves and there is even a tendency to suppose that nearly all colored aromatic derivatives contain a quinoid ring. But these views require to be reconsidered in view of the recent discoveries on the one hand of quinoid substances (like the imines) which are colorless, and on the other of colored bodies closely resembling the supposed quinoid) aromatic colored compounds, which cannot contain a quinoid ring because they are not aromatic derivatives at all.

"The causes which determine the absence of color among these quinone derivatives are not understood. It seems certain that the simple quinoid compounds form two series, one colored, like the quinones themselves, and the other not. On the other hand, these bodies are capable of a further increase of color, which must be accompanied by some structural change. In the triphenyl-methane series, for example, the feebly colored Homolka bases go over on treatment with acids into the brilliantly colored dyes. This is generally represented as the passage of trivalent into pentavalent nitrogen:

$$(H_2N.C_6H_4)_2C = C_6H_4 = NH \longrightarrow (H_2N.C_6H_4)_2C = C_6H_4 = NH_2Cl.$$

But there is much evidence to show that the change of valency of the nitrogen is not sufficient to determine color: thus the diimine salts are colorless. It is clear that the influence of a pentavalent nitrogen atom on the color depends largely on whether it has a hydrogen atom attached to it: if it has, then the effect on the color is much the same as if it was trivalent; if it has not, then its effect is usually quite different. The conversion of the group $—NX_2$ where X is a hydrocarbon radical, into $—NX_2HCl$ does not seem in general to influence the color, but its conversion into $—NX_3Cl$ does so in a very marked way. Of this we have an example in the quinone imine derivatives which we have just been considering, and another (curiously in the opposite direction) in rosaniline dyes, where the change from $—NEt_2$ to $—NEt_2HCl$ is without effect, while the change to NEt_3Cl destroys the influence of this group on the color altogether. This is one of the phenomena which suggest that there is a difference in constitution between bodies of the type R_3NHX and those of the type R_4NX.

"We must therefore look for some other change of structure in the conversion of the Homolka bases into the rosaniline dyes. In this connection certain facts recently discovered by Willstätter with regard to the quinone-diimines are of great interest. If unsymmetrical dialkyl-*p*-phenylene-diamine is oxidized, brilliantly colored substances are produced, known from their discoverer as Wurster's salts, which were supposed to be true diimine derivatives, *e. g.*, $HN = C_6H_4 = N(CH_3)_2Cl$. Further investigation has shown, however, that these bodies contain an atom of hydrogen more than this, they are bimolecular compounds (analogous to the quinhydrones) of one molecule of the oxidation product with one molecule of the unoxidized diamine, and may be written:

$$\begin{array}{lcl} NH_2Cl & . \ . \ . & NH_2 \\ \| & & | \\ CH_4 & . \ . \ . & C_6H_4 \\ \| & & | \\ N(CH_3)_2Cl & . \ . \ . & N(CH_3)_2. \end{array}$$

the dotted lines indicating some unknown kind of linkage. If they are further

oxidized to the true diimines the color disappears. Willstätter suggests that this peculiar linkage, which he calls meriquinoid (partially quinoid), is the cause of color in bodies of this type. An analogous explanation would hold for the triphenylmethane dyes, the true dye having a linkage between the quinoid nucleus and one of the other nuclei, which would be absent in the Homolka base."

On p. 92 there is an interesting paragraph in regard to the imido chlorides.

"In the case of the α-oxy-acids, such as glycollic acid, it was formerly supposed that the ture imido-acids could be isolated. Glycollic acid gives a normal amide $CH_2OH.CO.NH_2$; but if its anhydride is treated with ammonia, or its imido-ether is saponified, an isomeric substance is obtained, which was originally assumed to be the iso-amide or imidohydrine $CH_2OH.C\begin{matrix}OH\\ \diagdown\!\!\diagup\\ NH\end{matrix}$.

"Analogous compounds have been obtained from other α-oxy-acids. The subject has been reinvestigated by Hantzsch and Voegeln, who have shown that the properties of these substances are incompatible with this structure—and, indeed, as far as one can see, with any structure. They cannot be converted into the amides, a change which one would expect to occur with the utmost ease, and their molecular weight is twice that required by the simple formula. Their other properties are also most extraordinary. Though they are only weak bases, and are not acidic at all, their solutions are very good conductors of electricity, so that their electrolytic behavior is that of salts. Moreover, though they are fairly stable to acids, they are easily decomposed by certain salts, such as calcium chloride, with the formation of a glycollate. No satisfactory hypothesis has yet been proposed to account for these phenomena."

It is worth while noting that nitroso-butane, p. 122, has a sublimation point below the melting point, 76°.

Somebody should certainly work out more carefully the conditions determining the production of red and yellow salts, p. 174, from the nitrophenols.

Under fulminic acid, p. 224, we find the following:

"The overthrow of all two-carbon formulae and the final establishment of our knowledge of fulminic acid on a firm basis, is due to the work of Nef. He showed in the first place that all the evidence was in favor of its containing only one-carbon atom in the molecule. Its decomposition products are nearly all one-carbon bodies. It is formed, as we have seen, by treating sodium nitromethane with mercuric chloride, and if treated with nitrous acid it is converted into methyl-nitrolic acid $H.C(NO_2)NOH$. If we take it as proved that there is only one carbon atom in the molecule and also consider the fact that on treatment with hydrochloric acid it gives hydroxylamine, only one formula is possible, namely $H.O.N = C^{IV}$. The real reason which prevented the earlier investigators from adopting such a one-carbon structure as this was their unwillingness to admit the existence of a dyad carbon atom. But this objection has been removed by Nef's other work on dyad carbon, and he has been able to show that his formula is alone capable of explaining the very remarkable reactions of fulminic acid, while all subsequent work on these bodies has only served to confirm his views."

"The one thing needful to establish Nef's formula beyond all doubt is a determination of the molecular weight. If it can be shown that fulminic acid con-

tains only one carbon atom in the molecule, we have no alternative but to accept Nef's view as to its structure. A direct determination of this magnitude is impossible, but indirect evidence of great force has recently been adduced, from the electrolytic behavior of the sodium salt in aqueous solution. The salt can be prepared by treating mercury fulminate in alcohol with sodium amalgam, and is fairly stable. On Nef's theory it is the salt of a monobasic acid NaONC; on any other, the acid is dibasic, and the salt $Na_2(ONC)_2$. Now van't Hoff has shown that the alkaline salts of mono-basic acids in fifth to tenth normal solution give a value of the dissociation factor i of about 1.85, and those of dibasic acids about 2.5. From this it follows that if sodium fulminate is NaONC, its apparent molecular weight in solution should be 35, but if it is $Na_2(ONC)_2$, it should be about 52. From the depression of the freezing point in fifth-normal aqueous solution, it was found to be 34.9, agreeing with that required for the monomolecular formula. Again Ostwald found that the increase in molecular conductivity in passing from N/32 to N/1024 solution, for the salt of a monobasic acid was from 4 to 8 units, and for that of a dibasic acid about 11. The observed increase for sodium fulminate was 5 units. These results make it certain that the acid is monobasic, and has the formula HONC; and hence Nef's view as to its structure must be adopted."

In the chapter on uric acid there is a delightful paragraph, p. 318, on the work of Medicus.

"In 1875 Medicus published a most remarkable paper on the constitution of this group of compounds. He produced hardly any new facts; but sometimes on the basis of facts already known, and sometimes, apparently, on no basis at all, he suggested formulae for nearly every known compound of the group—uric acid, xanthine, caffeine, theobromine, guanine, and hypoxanthine. The singular point is that with the exception of the position of one of the methyl groups in theobromine, all the formulae which Medicus proposed are absolutely correct; although it was not until the most recent work of Fischer, in which he revised and modified many of his own previous formulae, that they were recognized as being so."

On p. 378 we get a tentative explanation of the catalytic action of mercury on the oxidation of naphthalene by sulphur trioxide.

"The catalytic influence of the mercury, which occurs in other cases of sulphonation as well, is remarkable, and a very probable explanation of it has been given by Dimroth. He has shown that if a mercury salt is heated with an aromatic derivative, a compound is formed in which one hydrogen on the ring is replaced by mercury. This subsitution is quite peculiar in that the position taken up by the mercury is not determined by the substituent already present: it is always ortho. Now it is found that if benzoic acid is sulphonated in the presence of mercury, the amount of meta and para acids produced is the same as if the mercury were not there; but in addition a considerable quantity of the *o*-sulphonic acid is formed, which is not obtained at all in the absence of mercury. This shows that the catalytic influence of the mercury is due to the formation and decomposition of a mercury derivative, as it introduces the sulphonic group at the position which the mercury (but no substituent) would occupy."

Wilder D. Bancroft

THE PHOTOGRAPHIC PLATE, V

BY WILDER D. BANCROFT

SOCIÉTÉ CHIMIQUE DE FRANCE BIBLIOTHÈQUE

The Latent Image I

When light is allowed to act for a short time upon a photographic plate or upon silver bromide precipitated from aqueous solution, the silver bromide is changed in some way, because a so-called developer causes the silver bromide which has been exposed to light to blacken more rapidly than the silver bromide which has not been exposed.[1] We say that the light has produced a latent image and our problem now is to find out what change has taken place and what the latent image is. The difference between the exposed and unexposed portions of the plate is one that can be varied within fairly wide limits by treating the plate with certain reagents. When studying the chemical reactions, it is often advantageous to use a collodion plate instead of a gelatine one because collodion is less readily attacked than gelatine by most reagents.

The latent image is destroyed by nitric acid, the attack being more rapid the more concentrated the acid.[2] It is also destroyed[3] by chlorine, bromine, or iodine; by ferric chloride, cupric chloride, mercuric chloride, or gold trichloride; by chromic acid, potassium persulphate, acidified potassium permanganate, or potassium ferricyanide; by hydrobromic acid, hydrochloric acid, potassium iodide. In other words these substances attack the material composing the latent image more readily than they do the unexposed silver bromide. On the other hand sodium thiosulphate dissolves the unexposed silver bromide more rapidly than the silver bromide which has been exposed to light. The same general statement is true, though to a varying degree in regard to ammonia, to potassium cyanide, and to ammonium bromide.[4]

[1] Cf. Englisch: Eder's Jahrbuch der Photographie, 15, 605 (1901); Schaum and Braun: Ibid., 18, 74 (1904).

[2] Eder: Sitzungsber. Akad. Wiss. Wien., 114, IIa, 1159 (1905).

[3] Eder's Handbuch der Photographie, 5th Ed., 3, I, 72 (1902).

[4] Eder: Jour. Phys. Chem., 13, 63 (1909).

In certain cases the latent image will be destroyed by processes taking place in the film under ordinary conditions. This phenomenon has been studied with some care by Baekeland from whom I quote.[1]

"One of the many practical advantages of the gelatine dry plate over the older processes consists in the fact that development of the plate can be postponed to any convenient time after the exposure. Examples have been recorded where negatives were successfully developed a number of years after the plate had been exposed in the camera. On the other hand, the question has often been raised in how far results obtained thus are inferior to those which are produced on plates developed immediately after exposure. Direct facts have been given indicating a gradual disappearance of the invisible photographic image.

"The study of this question requires more accurate methods than those ordinarily resorted to by the average photographer and this may account for the reason why this question has brought out some quite contrary statements.

"The gradual disappearance of the latent photographic image seems to be a process exactly the reverse of the one which produces this image under the action of light. I propose to designate this phenomenon under the name of photo-retrogression. Very probably we have to deal here with what is called in chemistry a reversible reaction, similar to those occuring in all phenomena of dissociation and double decomposition where under the action of opposing energies which try to produce two different systems a condition of equilibrium is reached.

"That such a condition of equilibrium may exist has been shown conclusively by the study of photodecomposition of pure chloride of silver in sealed glass tubes, but an almost virgin field of study and research is still open for the physico-chemist who desires to determine the limits and factors of photodissociation of various chemical compounds. Such

[1] Baekeland: Internat. Kongress angew. Chemie, Berlin, 4, 403 (1903).

study should not be limited to silver salts of which the susceptibility to the action of light is well known. Much more stable inorganic compounds may undergo profound changes as I have been able to show when studying the photooxidation of hydrochloric acid. This reaction is so much the more remarkable because hydrochloric acid, in presence of oxygen oxidizes under the influence of sunlight, whereas we know also that chlorine in watery solution evolves oxygen and forms hydrochloric acid. We are here in presence of a reversible reaction produced under the influence of light and analogous to what occurs in photoretrogression:

$$_2HCl + O \rightleftarrows H_2O + Cl_2.$$

"I shall not try to decide here what chemical reaction occurs in the production of the latent silver image, nor of its photoretrogression. I consider any decisive opinion on this subject as idle talk as long as we can not dispose of more thorough and complete laboratory investigations than the meager work which has been published on this subject.

"Without going into further general theoretical speculation, we may state that photoretrogression was known to exist long before the dry plate was invented. In the daguerreotype process the image can only be retained in proper developable state during a few hours. For the wet collodion process a similar fact is known, although it might be ascribed here to the physical condition of the sensitive layer which requires a certain degree of moisture. Photoretrogression in gelatine dry plates can best be observed in such cases where the time exposure has been limited to the very minimum, as for instance in undertimed negatives. Even then it may be difficult to observe it unless under some particular conditions. In all cases where more than enough exposure has been given, photoretrogression becomes much less apparent and this is perhaps the reason why so many contradictory statements have been made on this subject.

"I have studied photoretrogression on dry plates, films, bromide papers, and chloride papers. For all of my experi-

ments I take a standard negative purposely selected so as to show delicate graduations with no high lights and no transparent parts. I also use a sensitometer scale, similar to what is used for ordinary sensitometer tests, and consisting mainly of a glass plate divided into numbered squares made up of different thicknesses of opaque pigment. As source of light, I use a normal candle, the same quality of candle being used in all my experiments.

"In order to minimize the errors of observation, the experiments have always been repeated at least four times. My way of proceeding consists in placing the strip of dry plate, film, or paper in direct contact with the negative or sensitometer scale, and then exposing it during a given time at a constant distance from the candle light. All ordinary precautions are taken so that the experiment should only take place when the flame of the candle burns under normal conditions.

"In each series of experiments, some of the dry plates, films or papers are developed immediately, the development being carried as far as possible; *i. e.*, until the image does not gain any further strength. The results thus obtained are numbered and stored away for further comparison. An equal number of the dry plates, films, or papers exposed under the same conditions are stored away in the dark, undeveloped but are treated with the same developer afterwards at specific intervals. Proper precautions are taken while storing the tests, so as to exclude the possibility of outside influences on any of the light-sensitive material. When developing any of these tests a developer of strictly the same composition and same temperature is taken and development is carried on under exactly the same conditions, but in each case, development is carried on as long as the image gains in strength or detail, regardless of beginning 'fog.' In each case I selected a developer which experience had indicated to be best adapted for each sensitive material.

"Some of the experiments were repeated using different developers but in each case the results were only compared with those obtained by identical developers. I have observed,

however, that whenever photoretrogression was apparent, it would be shown by each one of the developers, so that the nature of the developer seems to play no role in this phenomenon. In the first experiments, thus conducted, I came soon to the conclusion that certain varieties of films and bromide papers, also some chloride papers show photoretrogression to considerable extent, even after relatively short intervals, while other varieties and specially dry plates do not show it so much. This is mainly due to some chemical differences in the emulsion as will be explained further. In some varieties of bromide paper and films, photoretrogression was quite apparent, even after so short a time as forty-eight hours. The image developed after this time was invariably weaker than the one obtained after exposure; at the end of a few days the results became much more decisive and after two month in some cases only a faint image was all that the developers could bring out.

"Let me repeat here and insist on what I have stated before, that these results become apparent only in such cases where exposure has been insufficient and where consequently the prints have been undertimed. In such cases, only, development can be carried on to its full limit, and after all silver salts, which have undergone the action of light, have been reduced, the image will not gain any further strength, even if the developer is left in contact for a considerable time. The only effect which such prolonged development may then produce is a general gray 'fog' which covers the whole image without strengthening it or changing the relative density of the different parts of the first developed image.

"In full timed prints and by these we designate such ones as have practically received a slight excess of exposure, this condition of affairs does not exist; by developing these we reach a stage where development has to be stopped, not on account of fear of 'fog' but because the shadows and half tones will acquire too great a density, which would prove objectionable in a negative and which in our experiments renders it impossible to distinguish slight differences in the

results. All experienced photographers will rather give too much than too little exposure to their negatives. This practice is very commendable in view of the fact that thereby the effect of photoretrogression is avoided.

"However, there are many cases where full timed exposures are not possible, for example, in instantaneous work and there photoretrogression may have serious drawbacks. It may become objectionable still in some methods of automatic printing and developing which are carried out now-a-days on a large scale by some industrial establishments. As the amount of material involved in one of these operations may represent thousand of dollars, at a time, it is quite natural that in such cases photoretrogression deserves special attention.

"A few years ago when automatic printing and development or 'photography by the mile,' was first carried on in New York, it was brought to my notice that a large roll of bromide paper about 500 meters long and 65 cm wide, which had been printed automatically by artificial light, could not be developed to the proper strength, although the test strip which had been printed under identical conditions, but developed immediately afterwards, had given excellent results one week before. The timing device of the automatic printer, the steady quality of the light, the uniformity of sensitiveness over the full length of the paper and the conditions of the developer were all critically examined. At the time, I had just started my investigation of photoretrogression and I was able to trace to this phenomenon the difference in results. That this was really the cause of all the trouble was proven beyond doubt by some direct experiments which were made afterwards.

"Mr. A. E. Johnstone, of New York, reported to me similar cases which have been observed lately during the development of strips of negative and positive films such as are used now-a-days for animated photographic exhibitions. For instance, a large roll of films exposed in Europe and of which a test strip had been developed there so as to make sure that the exposure was correct, was shipped to New York for fur-

ther development. On arrival there, it was found that the pictures developed were so weak as to make the results unsatisfactory. The same developer was used as in Europe and great stress was put on the quality of the chemicals, but without avail. Finally the undeveloped portion of the film was reshipped to Europe to the party who had developed the trial strip, but he could not obtain any better results.

"Another case was cited to me of an undeveloped film which was sent to New York from the Philippine Islands. This film had also been exposed in an apparatus for animated photographs, and by a competent operator who tested a portion of the strip for exposure and development. On arrival in New York, the image could not be developed, and showed all signs of photoretrogression. In this particular instance, the film had been submitted for a relatively long time to a humid and warm climate, which includes conditions which are most favorable for producing photoretrogression as we shall see later.

"I have tried by direct experiment to determine what factors have an influence on photoretrogression.

Temperature.—Dry plates, films, bromide paper and chloride paper were exposed as indicated above. A certain number of the tests were developed immediately, a same number of them were enclosed in a bottle provided with a glass stopper and kept in a refrigerator at a temperature ranging from 1° C to 4° C. An equal number of the tests were kept during one week in a stoppered glass bottle in a box of which the temperature was kept at 40° C to 48° C. At the end of three days photoretrogression was very apparent for the tests kept at a high temperature, whereas it was not noticeable even after two weeks for the tests which had been stored in the refrigerator.

Humidity.—Same tests as above were repeated. Some were placed in a large earthenware jar provided with a tight cover. In the center of the bottom of the jar was placed a large cylindrical glass containing sulphuric acid 66° Bé. so as to keep a very dry atmosphere. Other tests were placed in a

similar jar but, instead of sulphuric acid, the glass this time contained cotton, soaked with distilled water so as to saturate the air of the jar with humidity. The two jars were left in a room of which the temperature oscillated between 18° C. and 27° C. At the end of two weeks, the tests of both jars were developed. All showed photoretrogression, but the tests in the humid jar showed it much more than the ones contained in the dry atmosphere.

Chrome alum.—In all above experiments I had the opportunity to observe that some dry plates which I used, showed less photoretrogression than some films, bromide papers and chloride papers. Then again, films and bromide and chloride papers of different makes showed results quite different with each brand. I soon found out that those papers which were most subject to photoretrogression had either a slight acid reaction or contained noticeable amounts of chrome salts. In order to determine in how far the presence of chrome salts has an influence on this phenomenon, I made a bromide emulsion and after dividing it in two portions I added to one of these about 1% chrome alum of the amount of gelatine used in the emulsion. The other portion received no addition and both emulsions were used to coat some test plates and papers. The tests were dried under the same conditions, and afterwards exposed and developed at long intervals. Photoretrogression was much more apparent with the tests containing chrome alum than with those without this salt.

Acidity.—In the previous experiment, I noticed that the tests which contained chrome alum showed a slight acid reaction on litmus paper. In order to determine whether acidity or chrome alum has the greater influence on photoretrogression, I repeated the experiment in the following way: To the whole of the emulsion I added the same amount of chrome alum. Then I divided the liquid into two portions. One of the portions was used to coat test plates just as it was; the other received an addition of some drops of diluted ammonia, just enough to produce a very slightly alkaline reaction. An initial test showed little or no difference in the sensitiveness of

both emulsions, but after a few weeks, photoretrogression was less apparent in the tests which were quoted with the slightly alkaline reaction. I next compared a neutral emulsion containing chrome alum with the same emulsion, containing no chrome alum, but enough citric acid so as to give it a distinct acid reaction. The acid emulsion without chrome alum produced more photoretrogression than the neutral emulsion with chrome alum.

"In all these experiments the tests were carried on in the same way and kept under the same conditions for each set of experiments, but in certain cases development of all the tests of each set had to be postponed for a more or less longer period until such time was reached when the difference in the results was sufficiently apparent to enable me to draw conclusions. These experiments explain why certain brands of dry plates, films or papers show more photoretrogression than others. This phenomenon must undoubtedly be attributed to slow chemical action and the chemical conditions of the different emulsions determine the speed and intensity with which it occurs.

"It is a known fact that emulsions which are intended for films or papers receive almost always an abundant addition of chrome alum, so as to render the gelatine coating less soluble and to produce at the same time a more viscous liquid which is better adapted for certain coating machines. Dry plates, on the other hand, require no such addition of chrome alum.

"Furthermore, if emulsions are made by the 'boiling' process where the 'ripening' is obtained by a prolonged application of heat, their final reaction will be neutral or very slightly acid and the smallest amount of chrome alum may give them an acid reaction. Emulsions 'ripened' with the ammonia process will almost always be alkaline even after long washing, and the addition of a little chrome alum will not necessarily give them an acid reaction.

"I should mention here that emulsions, made with the ammonia process but separated by a centrifugal machine,

may produce, after reincorporation of the silver bromide with fresh gelatine, a neutral or slightly acid reaction which may become apparent after the addition of chrome alum. Let me also call attention to the fact that these slightly acid or neutral emulsions give generally papers or dry plates which have better keeping qualities and which are less liable to become 'foggy' with age; it so happens that such emulsions are also those which are most liable to show photoretrogression.

"In the above statements, whenever I referred to chloride paper, I meant papers of the Velox class coated with such emulsions which contain chloride of silver in the gelatine, but without any excess of nitrate of silver or any other soluble silver salt, and which are intended to produce images by alkaline development and not by printing out methods.

"The facts mentioned here add new strength to the supposition that the latent photographic image is due to a chemical and not to a physical condition. Many hypotheses, none of which has been sufficiently demonstrated, have been proposed to explain this subtile chemical reaction. Whether we try to explain the latent photographic image by the formation of free silver, sub-bromide and sub-chloride of silver, or again by the existence of oxy-sub-bromides or oxy-subchlorides, the above-mentioned facts point out that photoretrogression occurs by chemical action. This action is probably the reverse of what occurs in the formation of the latent image. Whether in this phenomenon oxygen, directly or indirectly plays a role, we cannot say yet, and further work in this direction may give us a better insight in this matter; but I call your attention to the fact that a neutral or alkaline light-sensitive layer would be in better condition for absorbing free bromine or chlorine or oxygenated derivatives of the same, than if it had an acid reaction.

"As far as regards the influence of heat and moisture, it is sufficiently accepted as being of great importance in all chemical reactions; in this particular case we are not astonished to see again the two factors as being of very marked influence in photoretrogression.

"Photoretrogression, or slow disappearance of the latent photographic image, takes place in glass plates, films and paper coated with gelatine silver bromide or gelatine silver chloride.

"Photoretrogression is especially apparent in undertimed images and much less noticeable in overtimed images.

"Photoretrogression may, under special conditions, become apparent in dry plates, films or paper, forty-eight hours after exposure, and may increase until the latent image has nearly disappeared. Photoretrogression occurs quicker at high than at low temperatures.

"Photoretrogression is less apparent in neutral or slightly alkaline sensitive layers than in such ones which have an acid reaction."

Barker[1] found that when plates, made from a well-washed silver bromide emulsion are packed after exposure in Swedish filter paper and yellow paper, the latent image does not disappear in eight years. If the exposed plates are packed in yellow paper alone, fog is formed. The latent image disappeared rapidly if as much as 1/480 part of potassium iodide had been added when the emulsion was prepared. Potassium bromide also increased the rate of disappearance of the image though not very much. Ammonium chloride acted in the same way. If the emulsion contained 1/240 part of tannin, the image could be seen faintly before development. The presence of tannin prevents the disappearance of the latent image.

In some photometric work carried on by Brush[2] it, was found that "photographic action is slow in starting, involving considerable light energy which leaves no permanent record. If exposure is stopped at this stage, the starting action relapses almost wholly within a few minutes and is lost to further exposure. Once started, however, action increases rapidly to full activity and then remains substantially constant dur-

[1] Eder's Jahrbuch der Photographie, 19, 364 (1905).
[2] Phys. Rev., 31, 241 (1901).

ing further exposure. Relapse of sensitiveness follows exposure and is very marked at the end of a few hours.

"Photographic action, when fully excited, *continues many minutes after exposure*, gradually dying out. With the adopted period of exposure, this after action amounts to something like eight or ten percent of the whole. Within an hour or two after action has ceased, relapse sets in and amounts to about four percent in the first thirty hours, fully half of which occurs within the first four hours."

Lüppo-Cramer has also made some experiments on photo-retrogression[1].

"I have shown previously that the decay of the photochemical action is especially marked with iodides of mercury, that this reaction velocity is increased enormously by moisture, and that the recombination of the dissociated halogen with the mercury, taking place under the influence of water, is more complete the finer the grain of the emulsion. The decrease of the blackening with dry mercurous iodide gelatine also takes place very much more rapidly and more completely with a fine-grained unripened iodide than with the ripened emulsion. If one exposes one plate of each type until they are blackened to about the same degree and then puts them away in the dark, it is easy to notice a great difference at the end of a day or two. At the end of two days the fine-grained mercurous iodide has become very light while the coarser emulsion shows only a slight decrease in color. At the end of seven days the fine-grained emulsion has entirely recovered its original bright color while the coarser mercurous iodide is still very dark.

"Stimulated by this experiment I decided to see whether a fine-grained silver bromide emulsion might not show the phenomenon of the decay of the latent image even though the highly sensitive bromide does not show it to any appreciable extent. As a matter of fact water causes a distinct decrease in the darkening of a fine-grained silver bromide emul-

[1] Lüppo-Cramer: Phot. Correspondenz, 44, 130 (1907).

sion caused by exposure to direct sunlight. Nothing of the sort can be detected with highly sensitive plates. It is a question whether the decrease of the blackening with fine-grained plates is really due to a recombination of the halogen with the silver similar to that with the iodides. There is no doubt but that the latent image fades appreciably in these fine-grained emulsions, though slowly as is the case with all latent images.[1] A large number of plates of the same fine-grained emulsion as that used in a previous investigation were exposed under a negative to daylight for the same length of time. Immediately after exposure half of each plate was developed, using in every case the same developer at the same temperature and developing for the same length of time. The developed halves were then put away together with the undeveloped halves. At the end of two months a marked decay of the latent image could be detected; at the end of six months only the high lights were left. There was no marked difference to be detected between plates developed after nine months and plates developed at the end of six months. There is therefore a distinct decay of the latent image on silver bromide gelatine plates when the emulsion is a fine-grained one."

The phenomena of the latent image can apparently be duplicated in other ways without exposure to light. A dilute solution of a reducing agent will affect a dry plate in such a way that the silver bromide can then be reduced by the ordinary developer under ordinary conditions. Namias[2] has shown this for solutions of stannous chloride.

"In a communication I made to the Chemical Society of Milan in 1897 on the chemical reactions involved in the manufacture of silver mirrors, I made use of a fact which has appeared to me to be a very interesting one.

"If one takes a carefully cleaned mirror and pours upon it a solution of stannous chloride, even one as dilute as

[1] Cf. Lüppo-Cramer: Phot. Correspondenz, 43, 80 (1906).
[2] Phot. Correspondenz, 42, 155 (1907).

1 : 100000, and if one then washes the mirror with distilled water, the rate of precipitation of silver from an ammoniacal tartrate solution is much greater with such a mirror. The infinitesimal amount of stannous chloride remaining on such a plate is sufficient to make the reduction of the silver considerably easier. The labile equilibrium of the ammoniacal silver tartrate solution is at once upset by the action of infinitely small traces of such a powerful reducing agent as stannous chloride.

"When I experimented to see how the same substance acted towards silver salts in developing the latent agent, I found that its effect was quite marked. In fact a 1 : 20000 solution of crystallized stannous chloride, $SnCl_2.2H_2O$, in distilled water, completely free from air, will produce in a few minutes' action on a silver bromide plate a latent action which can be detected by developing with an ordinary developer. The action of stannous chloride seems to be exactly analogous to that of light.

"If one allows a sufficiently concentrated solution (1% for instance) to act for an instant, or a more dilute solution for a longer time, one obtains a latent image which develops with great sharpness. If the action of the stannous chloride lasts too long, one gets a result analogous to that caused by over-exposure; the plate fogs and there is no sharpness. This is the result, for instance, if the one percent solution is allowed to act for two or there minutes. If the solution is allowed to act longer, it causes a visible change just as light does."

This result has been observed by Perley[1] who has also duplicated the action of light by means of a sodium arsenite solution or by a diluted solution of an ordinary developer.

Carey Lea[2] has shown that a moderate pressure apparently produces a latent image.

"I was able to show many years ago that mechanical force could produce a latent image. Lines drawn with a

[1] Jour. Phys. Chem., 14, 689 (1910).
[2] Am. Jour. Sci., [3] 43, 528 (1892).

glass rod on a sensitive surface could be rendered visible by development in the same way as impressions of light. An embossed card pressed on a sensitive film left an invisible image which could be brought out by a reducing agent. The raised portions of the embossed work exert a stronger pressure on the sensitive film than the rest of the card and these portions darkened when acted upon by a reducing agent. In the same way, the lines traced with a glass rod, blackened under a developer. In each case, it was the portions which had been subjected to pressure which yielded first to the reducer. It is therefore clear that in the molecules which had received this slight pressure the affinities of the atoms had been loosened."

Lüppo-Cramer[1] does not believe a true latent image is formed in this way. He says that the pressure phenomena "can be distinguished from real reduction phenomena because the latter occur throughout the whole film and are not changed in the slightest by any rubbing of the surface."

Carey Lea's experiments show that something similar to a latent image can be formed by heat.[2]

"To determine the effect of heat on silver bromide, pieces of bromide paper were placed in a desiccator (of course using inactive light), and heated to the extent indicated. For each piece so heated a corresponding piece cut from beside it in the same sheet was preserved and these two pieces, that heated (after complete cooling) and that not heated were placed side by side in an oxalate developer. Comparison between these developments indicated the effect of the heat. The following results were obtained.

"A piece kept for 3 minutes at 145° was strongly affected and blackened quickly in the developer, the companion piece remaining white. A piece kept for 15 minutes at a temperature commencing at 131° and ending at 136° was still more thoroughly affected than the foregoing, the longer expo-

[1] Phot. Correspondenz, 40, 180 (1903).
[2] Carey Lea: Am. Jour. Sci., [3] 41, 262 (1891).

sure more than making up for the lower temperature. Companion piece remained white. A piece kept for 8 minutes at a temperature 107° to 108° was distinctly but not strongly affected. Companion piece as before. A piece kept for 17 minutes at a temperature of 100° to 102° was almost unaffected. A long and careful development brought out a faint difference between the piece so heated and its companion piece.

"It was found that to obtain accuracy in determinations such as these, the paper must rest on a glass, and not a metal shelf in the desiccator, as the metal shelf is always hotter than the air by which the thermometer is affected. In using a metal shelf, if the paper curled by reason of the heat, the part that rested on the shelf developed darker than that which was simply acted on by the air. By substituting a glass shelf this difference of effect disappeared.

"The result of the foregoing and other experiments was that the effect of heat on AgBr commences at about 100°, that up to 108° it is still slight and acts slowly, but that at 120° to 126° a strong action commences, which further increases as the temperature is raised. The analogy with allotropic silver is well marked.

"It may at first seem strange that a temperature of 100° should produce a permanent change in a substance which will bear a high heat without decomposition, but the explanation lies in the presence of water in the former case. When silver bromide is formed in paper and dried in the air, it still retains moisture. Even at 100°, this moisture is not driven off. A silver haloid requires to be heated to a temperature between 130° and 140° for several hours before it ceases to lose weight. Therefore in all the foregoing cases, moisture must have been present.

"It remains to be shown that by a sufficiently long exposure to a moderate heat in the presence of moisture a visible decomposition results. For this purpose silver chloride was precipitated with an excess of hydrochloric acid, after thorough washing was placed in a glass tube of about a centimeter in

internal diameter and one half a meter long, and was sealed up with a blast lamp. During all these operations the chloride was thoroughly protected from light. Five or six cubic centimeters of pure water were first added to the chloride. It was intended to exclude completely the effect of pressure and to act on the chloride as far as possible by heat only, and for this reason a longer tube was used and one end only was immersed in the chloride of calcium bath, the other end remained cold throughout the operation.

"The silver chloride formed itself into a compact plug and was forced by the steam which generated below it up to the middle of the tube. This effect though not intended, answered very well as the chloride was kept constantly under the influence of steam at about 100°. It soon began to darken and at the end of three or four hours all the lower part was violet-brown, the upper part gray, the change taking place entirely through the mass. Some thin smears of silver chloride on the lower inside part of the tube were completely blackened.

"On opening the tube next day there was no escape of gas. The water sealed up with the silver chloride had acquired a faint but distinct alkaline reaction showing that enough alkali had been dissolved from the glass to overcome any acidity arising from decomposition of the chloride. The water contained traces of alkaline chloride.

"A similar examination was made with silver bromide precipitated with excess of hydrobromic acid and thoroughly washed with distilled water. The action of diffuse light on silver bromide is very different from that on silver chloride. A portion of that prepared, as above mentioned, changed in diffuse light very quickly from yellow to greenish yellow, but after that first change the alteration was extremely slow and in an hour had only reached to a dirty greenish gray. The action of direct sunlight was quite different; fifteen minutes exposure changed the greenish gray to dark chocolate-brown.

"In the tube, the silver bromide did not form a plug ike the chloride but separated into balls which remained in the

bottom of the tube. By keeping the chloride of calcium bath considerably above 100° the water in the tube was kept actively boiling: it condensed in the upper part of the tube and returned. Six hours of this treatment only brought the bromide to the same greenish color which it would have acquired by a few minutes' exposure to diffuse light.

"The conclusion to be drawn as respects both the silver haloids is that they undergo actual decomposition by the action of moist heat, but that this effect is much more marked in the case of chloride than that of bromide."

Carey Lea also found that sulphuric acid seems to produce a latent image.[1]

"Dilute sulphuric acid quickly changes allotropic silver to normal, and therefore if the parallelism which I have indicated really exists, marks made on bromide paper with dilute sulphuric acid should be capable of development.

"The experiment was made by drawing characters on silver bromide with a glass rod dipped into sulphuric acid diluted with twice its bulk of water. After allowing the acid to remain in contact for two or three minutes, the paper was immersed in running water and washed for an hour or two. On applying the oxalate developer nothing appeared. Feeling confident that an effect must be produced, the experiment was repeated several times and the results closely examined. On one specimen it was found that the characters had appeared, but reversed, that is lighter than the ground which had darkened by the development being pushed. This at once gave a clue; it showed that traces of the acid adhered too strongly to be removed by washing and by locally checking the development, interfered with the reaction. Accordingly, next time after a very short washing, the paper was immersed in water to which a trace of ammonia had been added, and after ten or fifteen minutes' action, the ammonia was thoroughly washed out. The result was striking: as soon as the developer was applied, the characters which had been traced with acid came out strongly as brown marks on a white surface.

[1] Carey Lea: Am. Jour. Sci., [3] 41, 264 (1891).

Cold sulphuric acid even undiluted is generally held to have no action on silver haloids, but it is well known that the hot, strong acid decomposes them. The foregoing experiments leave no doubt that the cold dilute acid produces an initial effect invisible to the eye but revealed by greater tendency to give way under the action of a reducing agent. This action of the acid comes therefore exactly into line with that of light and heat. In all three cases an effect is produced inappreciably until a reducing agent is applied. But in all three cases the agent which produced this invisible effect is capable by continued action under favorable conditions of bringing about a visible change without the aid of a reducing agent."

In the Waterhouse process for making positives, it has been shown[1] that thiocarbamide causes some change in unexposed silver bromide such that the bromide is readily reduced by the developer. In fact the change is so marked that unexposed silver bromide, after treatment with thiocarbamide, will often reduce more rapidly than silver bromide which has been exposed for a short time to light.

In the preceding pages I have referred to some of the more interesting characteristics of the latent image. We can now consider some of the theories in regard to the nature of the latent image. It has been believed that the latent image is an oxidation product; a physical modification; a silver nucleus; a sub-bromide; a solid solution.

The theory that the latent image is an oxidation product has not met with much favor; but it is always interesting to see how much of a case can be made out for any hypothesis, so I quote v. Tugolessow's paper in full.[2]

"The prevailing assumption in regard to chemical reactions in photographic processes is that the light-sensitive salt (usually a silver halide) is decomposed by light into a substance with a lower valence. This belief seems to be based on

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[1] Perley: Jour. Phys. Chem., 13, 655 (1909).

[2] v. Tugolessow: Phot. Correspondenz, 40, 594 (1903).

the behavior of silver chloride (AgCl) which loses weight while blackening in the light and changes so as to look like silver sub-chloride (Ag_2Cl).

"This might all be right to a certain extent if the only action of light on silver chloride was to cause an ever-increasing blackening. As a matter of fact something else is to be noticed. In addition to the change which can be followed by the eye, there is also an invisible change taking place which we detect in the case of silver bromide and silver iodide by means of a developer. There is reason for supposing that the invisible change precedes the one which is visible to the eye, and we must therefore assume that the production of a lower compound from the light-sensitive salt is not the immediate result of the action of the light but is merely the last stage in a more or less complicated process. The fact that all developers are reducing agents and that the haloid salts of silver form no saturated compounds, causes us to assume that the first action of light is not a reducing one but an oxidizing one. The lower stages may result from the decomposition of the substance with a higher valence which is first formed.

"According to this assumption the change of silver chloride in the light takes place in two stages; first, an oxidation to a higher valence; second, the decomposition of the new compound into silver subchloride or even into metallic silver. Since the first stage must be accompanied by an increase in the weight of the silver chloride, it seemed possible that the hypothesis could be checked experimentally. Well-washed silver chloride was therefore spread in thin films on watch-glasses, dried to constant weight at 100°, placed in a desiccator and exposed to daylight. At the end of an hour the glasses were weighed again and in all cases a distinct increase in weight was noticed. This was sometimes as high as 0.003 g per 1.995 g AgCl and was almost identical when referred to equal surfaces.[1]

"An experiment with silver bromide led to no satisfac-

[1] When the exposure to light was increased to eight hours a decrease in weight occurred.

tory blackening[1] even below 100° and the same thing happened in a second experiment. Nevertheless, the action of light caused an increase in weight of 0.0005 g and 0.0015 g per gram of silver bromide.

"The increase in weight of the silver chloride is strong proof that no decomposition has taken place and that a combination with some other substance has occurred. Under the condition of the experiment, the other substance must be the oxygen of the air and the new compound must therefore be one corresponding to silver peroxide. It is known, however that silver peroxide decomposes when heated to 150° and consequently one would expect that the silver halide changed by light would decompose when heated, and that the latent image would consequently be developed.

"To check this hypothesis an exposed collodion plate was heated for one to two hours in a drying closet at 125° and the result was exactly as expected. It was possible in this way to develop the latent image. If the fixing was carried out very carefully, it was possible to obtain a negative from which one could make quite clear prints upon light-sensitive paper.[2]

"This experiment is, therefore, to a certain extent an argument for the belief that the action of light causes an oxidation. Since an oxidation can only take place in presence of an oxygen carrier, the light-sensitive substance should not be affected by light in the absence of oxygen carriers. Since it was not possible for me to study the action of light on the halide salts of silver in a vacuum or in an atmosphere of an inert gas, I availed myself of a simpler method, but one which seemed equally certain to give a conclusive result.

"I covered the silver chloride with a solution of stannous chloride ($SnCl_2$) and exposed the whole to the light. Since stannous chloride is a reducing agent, there is no possibility

[1] Probably some light got into the dark room though the eye was not able to detect any leaks.

[2] It is only right to say that the fixing must be done very quickly or else the image may disappear.

of the silver chloride being oxidized and consequently it was to be expected that silver chloride would not blacken in the light under these conditions. As a matter of fact the silver chloride did not blacken though exposed to the light for several days. Even when the water evaporated and crystals of stannous chloride separated, there was no change in the color of the silver chloride.[1]

"Just the opposite was observed when hydrogen peroxide was substituted for the stannous chloride, in other words, an oxidizing agent instead of a reducing agent. The silver chloride darkened more rapidly and more completely than in the air or in the water, while silver bromide blackened fairly rapidly under the hydrogen peroxide solution, although ordinarily it is not easily changed.

"If the usually accepted view of the photographic process were correct, these experiments should have given the opposite results from what they did. The silver chloride and silver bromide should have been unchanged in the hydrogen peroxide solution and should have changed rapidly in the stannous chloride solution. Since this did not happen, it is clear that there can be no question of a reduction of the silver salts.

"If the photochemical changes are a result of oxidation, it follows that oxygen carriers would have the same effect as light upon the silver halides. To test this conclusion, silver chloride paper was exposed to the gases set free from bleaching powder by acids, chiefly hypochlorous anhydride and chlorine. It was assumed that the silver chloride paper would blacken as in light, if the silver chloride were oxidized under these conditions. As a matter of fact small dark spots, having a metallic luster, appeared after ten or fifteen minutes' exposure to the gases. If the gases acted for a longer time, the paper was bleached again but at the same time underwent a great loss of light-sensitiveness.

"This last experiment indicates that, in addition to the

[1] This experiment succeeds better the less stannic chloride ($SnCl_4$) there is in the solution.

change analogous to that produced by light, the silver chloride also undergoes another change which manifests itself in a decrease of sensitiveness to light. On the assumption that the latter change is due either to an absorption of hydrochloric acid by silver chloride or to the formation of a compound containing more chlorine, it would be necessary to limit the reaction so that silver chloride could react only with oxygen. This was accomplished by placing the silver chloride paper in an ozonizer and subjecting it to the action of the silent discharge. At the end of fifteen minutes the same dark spots appeared as before but they did not disappear on prolonged exposure to the silent discharge.

"If the blackening of silver chloride is caused by a reduction, these experiments show that it can only be as the result of a decomposition of the higher oxidation stages. The close similarity between these results and those due to the action of light, points to an identity of steps. So far as the silver halides are concerned, we are quite justified in breaking away from the generally accepted opinion in regard to the photochemical reactions. We should adopt the view that the reaction of light on the silver halides is primarily an oxidizing and not a reducing one.

"The phenomenon of solarization and the increased weight of exposed silver chloride show that under the influence of light there is a direct addition of oxygen to the silver halide. The following general formula may therefore represent the salts after the action of light:

$$\begin{matrix} AgX \\ (AgX)_n \\ AgX \end{matrix}\!\!\rangle O \quad (X = \text{halide}).$$

In this formula n varies inversely with the exposure to light. When the action of light is a maximum, n becomes zero and the formula is to be written:

$$\begin{matrix} AgX \\ \\ AgX \end{matrix}\!\!\rangle O.$$

This is the expression for a saturated halide oxygen compound of silver.

"We must assume that the oxygen compounds of silver chloride are very instable and that therefore it is scarcely possible under ordinary conditions to make a compound corresponding to this formula. Yet the oxygen compounds of silver bromide must be much more stable than those of silver chloride, while the silver iodide compounds are more stable than the corresponding silver bromide ones.

"It is well known that silver bromide is more sensitive to light than silver chloride. Consequently we should expect silver iodide to be more sensitive than the bromide. Judging from the literature this is not the case. In order to clear up this contradiction, I made a number of experiments. Three strips of the same kind of paper was soaked in normal solutions of the three salts: the first in a solution of potassium chloride, the second in a solution of potassium bromide, and the third in a solution of potassium iodide. To convert these potassium salts into silver salts, the three strips of paper were dipped in a five percent solution of silver nitrate, dried, placed side by side in a Scheiner sensitometer, and exposed for thirty seconds to the action of daylight.

"After the development it appeared that the silver chloride paper had scarcely been changed at all, that the bromide paper had changed up to the fifth division, and the iodide paper up to the fourteenth division. When a longer exposure was given, all three strips of paper underwent a change and the change in the silver iodide paper was as much greater than the change in the bromide paper as the change in this latter was greater than the change in the chloride paper. Consequently the silver iodide is the most sensitive to light and silver chloride the least sensitive.[1]

"While studying the action of light on other light-sensitive substances, a few experiments were made with mercurous salts and with ferric chloride. Ordinary writing paper was soaked in a saturated solution of mercurous nitrate, dried, and exposed under a negative to light. My idea was that, if the action of light were an oxidizing one, an insoluble

[1] [The experiments do not refer to a ripened emulsion. W. D. B.]

basic mercuric salt would form where the paper was illuminated and would remain on the paper after the unchanged mercurous nitrate had been washed out.

"The action of light produced no visible change in the paper; but when the paper had been washed in boiling water, the exposed places assumed a yellowish color which then changed to a dark gray, making the image fairly distinct. The theory was confirmed. Under the action of light there was formed a colorless, insoluble mercuric salt which was changed by a large excess of water into the yellow salt, $Hg(NO_3)_2.2HgO.H_2O$. This latter reacted with the excess of mercurous nitrate in the solution, forming mercuric nitrate and mercurous oxide. The mercurous oxide was decomposed by boiling water into oxygen and metallic mercury.

"The action of light on mercurous chloride was also studied. Sheets of paper were soaked in a solution of mercurous nitrate, dipped in a dilute solution of hydrochloric acid, dried, and exposed under a negative to light. The action of the light was to be detected by means of the mercuramide compounds. Since those of the mercurous salt are black and those of the mercuric salt are white, it was expected that ammonia would only blacken the parts which had not been exposed to light. The experiment did not turn out at first as had been hoped for the whole sheet of paper was blackened by ammonia. After a short treatment with very dilute hydrochloric acid, the high lights became white. This shows that mercurous chloride is unquestionably changed to mercuric salt by light, but not completely: and consequently the test was spoiled by the ammonia reacting with some of the undecomposed mercurous salt. Since the amount of this latter was not large, a very short exposure to acid was sufficient to remove it, while the acid had practically no more effect on the portions which had not been exposed to light.

"Although there are many more experiments to be made on the chemical changes which take place under the influence of light, the facts which have been presented justify the con-

clusion that the action of light always tends to be an oxidizing action."

The accuracy of these observations has been questioned by Lüppo-Cramer,[1] who immersed silver bromide, silver chlorbromide and silver chloride dry plates in: water; three percent hydrogen peroxide; three percent sodium nitrite; and three percent stannous chloride. Hydrogen peroxide retarded the blackening in light, while stannous chloride and sodium nitrite caused a marked increase in the rate of blackening.

It is only fair, however, to point out that v. Tugolessow's experiments were made with silver chloride, bromide, and iodide precipitated in paper and that he did not work with dry plates. It is also fair to note that Lüppo-Cramer[2] has recorded the fact that a five percent sodium nitrite solution retards the blackening of silver chloride by light.[3]

Chapman Jones[4] is one of the enthusiastic supporters of the belief that the latent image is merely a physical modification of silver bromide.

"It is generally considered that the main question is whether a chemical or physical change takes place in the silver salt (silver bromide) when a developable image is produced. A physical change is an alteration in the nature of the substance which does not affect its composition. Silver bromide, when physically changed, remains silver bromide, but the nature of the combination of molecules into aggregates is modified. A chemical change consists of an alteration of the composition of the substance. In this case it would be a matter of decomposition; the silver and bromine, instead of remaining combined, would be wholly or partially separated. Now a chemical change must be preceded by a physical change; there must be a movement or commotion within the molecule before actual decomposition takes place.

[1] Eder's Jahrbuch der Photographie, 18, 335 (1904).
[2] Phot. Correspondenz, 40, 97 (1903).
[3] Cf. Perley: Jour. Phys. Chem., 14, 700 (1910).
[4] Science and Practice of Photography, 374, 387, 382 (1904).

The question, therefore, is not whether the change is chemical *or* physical, but whether it is physical only, or whether it passes beyond the physical stage to an actual decomposition. There certainly is some change, and, therefore, there is a physical change; but while some consider that this is followed by decomposition, others, including the author, consider that the balance of evidence is overwhelmingly against decomposition."

"If there is decomposition, the amount of silver salt that is decomposed must be exceedingly minute, small almost beyond imagination. The amount of decomposition might be increased many thousands of times before the products of decomposition would have accumulated in sufficient quantity for direct recognition. The exceeding minuteness of the extent of the decompostion is allowed, as it must be, by all who advocate the decomposition theory, but it is a very weak point in that theory, as will be subsequently shown. If the change is regarded as physical only, this difficulty disappears altogether, and the quantity of silver salt changed into the developable condition is readily recognized and weighable.

"The remarkable stability of the developable image has been adduced as an argument in favor of its consisting of a substance that is chemically, and not merely physically, different from the original silver bromide. But there is no reason why a physically changed silver bromide should not be as stable, or even more stable, than the sub-bromide. The soluble and insoluble varieties of sulphur remain soluble and insoluble respectively for long enough. The black and red sulphides of mercury are chemically identical, and both are stable. The same may be said of the yellow and red oxides of mercury. And each of these substances, it may be noted, behaves to certain reagents in a different manner from the other, though both, in each case, have the same composition. Many other examples might be quoted. On the other hand, many of the products of chemical change are exceedingly unstable.

"The stability of the developable image is not much argument either for or against either theory of the nature of the developable image, but what little weight it has, appears rather to favor the physical theory. An exceedingly minute amount of metallic silver or silver sub-bromide would probably be more readily affected by outside adverse influence than a physically modified silver bromide present in relatively very large quantity. Moreover, the silver or the sub-bromide is in any case, accordingly to the chemical theory, in the immediate presence of the bromine that it has lost, and one cannot accept this theory without supposing that the bromine easily leaves the gelatine and returns to the silver, or else that aerial oxygen readily oxidizes the sub-bromide, as these are the only explanations of reversal that have been suggested to fit in with that theory. The stability of the developable image becomes, therefore, from this point of view, a strong argument in favor of the physical theory, because it is necessary that the image shall be unstable according to the chemical theory."

"The exceedingly minute amount of sub-bromide produced by ordinary exposure, according to the decomposition hypothesis, is allowed on all hands to be very, very far from sufficient to furnish by itself an image that can be seen or discovered in any way, except by allowing it to grow. This growth, which means the reduction to the metallic state of the silver bromide that has not been affected by light by the indirect agency of that which has, is a necessary adjunct to the decomposition theory. The physical theory is complete in itself, and needs no supplementing. But the physical theory is in no way opposed to the fact that, under some conditions, the image spreads during development, unexposed silver salts being reduced to the metallic state. The demonstration that the image spreads in this manner, therefore, is no proof of the chemical theory, though it removes a difficulty which, if it existed, would at once condemn the decomposition hypothesis.

"But in a gelatine plate, it has never been proved that

the image does grow more than an almost negligible amount (if at all), such, for example, as might interfere in the photographing of fine black lines. It is common experience that in the development of a gelatine plate a time comes when the 'development is complete,' 'the exposure effect is exhausted,' 'there is nothing more to get,' 'the density ceases to increase,' to quote a few common phrases. If the whole image, except an indescribably small fraction of it, is the result of this growth or spreading, why should the growth of the image stop while the developer is still on the plate, instead of going on until the reduction of the silver salt is complete, and the plate is evenly black all over? It has been suggested that this growth cannot extend from granule to granule in the gelatine, but only from one part to another of the granule, so that only these granules that have been affected by light by the production in them of a few molecules of sub-bromide are amenable to development. This refinement of the chemical theory appears almost equal to the surrender of it. It formed no part of the original idea, and that the exigencies of the case should require such a suggestion is evident proof of the difficulty found in applying the chemical theory to the results of every day work.

"According to the decomposition hypothesis of the nature of the developable image, all that the developer has to do is to reduce the sub-bromide that is produced by the action of light to the metallic state, this silver, by acting on unaltered bromide producing more sub-bromide, which is in turn reduced, and so on. The developer, therefore, simply reduces silver sub-bromide to the metallic state. This hypothesis obliges us to believe that there are some substances that can reduce silver bromide but cannot reduce the sub-bromide, or else these substances are of such a nature that the action of silver on silver bromide to form the sub-bromide cannot take place in the presence of their solutions. The first suggestion seems exceedingly unlikely. With regard to the second, it is known that development is not hindered by ammonia or by a solution of ferrous citrate and ferrous oxa-

late, but by mixing the two, the author has been unable to develop a developable image, although the silver salt was slowly and in the end copiously reduced. These difficulties and the need for these out-of-the-way suggestions do not exist if the physical theory is adopted. It is only what would be expected that some substances should be able to reduce the silver bromide that has been made less stable by the action of light without affecting the unchanged bromide, while other substances should be unable to discriminate between the altered and unaltered bromide. It is often the case that it requires much care to distinguish by chemical means between two different physical conditions of the same substances.

"If there is decomposition, that is, if the developable image consists of silver bromide that has lost a part of its bromine, then, as the function of the developer is to remove bromine (leaving the image in metallic silver), exposure and development ought to be to a considerable extent interchangeable. But exposure and development are not interchangeable, for exposure beyond a certain point makes development impossible.

"In some cases, however, it is otherwise. In exposing printing-out papers it appears that the exposure may be stopped at almost any time, and the image completed by development. This developable image, therefore, has not the same characteristics as the one we are considering. It may be urged that in printing-out papers, organic salts of silver are present, and act as sensitizers, that is, absorbers of bromine, but gelatine is a sensitizer, too, and will absorb large quantities of bromine.

"One of the most direct pieces of evidence against the decomposition hypothesis is furnished by the action of a solution of ammonia. This reagent, it is admitted, decomposes silver sub-bromide, leaving half the silver as metal. Therefore, taking cognizance of this reaction only, the application of ammonia to the plate first in development ought approximately to halve the speed of the plate, because the amount

of the metallic silver produced by its action would be one-half the quantity produced by the initial action of the developer, which according to this theory, reduces the sub-bromide entirely. Or if the speed of the plate is not so much affected, certainly development should be retarded by the previous application of the ammonia, because it would give only half the amount of metallic silver to start with. But as a matter of fact, applying the ammonia first, rather quickens development, and tends to increase the apparent sensitiveness of the plate.

"An ordinary solution of ammonia is a good solvent for finely-divided silver, the oxygen of the air dissolved in it taking part in the reaction. The previous application of ammonia should, therefore, not only straightway halve the amount of metallic silver that otherwise would be available, but at once begin to get rid of the other half by dissolving it. As the largest possible amount of silver is exceedingly minute, thousands of times smaller than the smallest quantity directly detectable, and so finely divided, withal, as to be invisible, the ammonia should quickly dispose of it. Now these effects of ammonia are not imaginary effects; they can easily be verified. But as a matter of fact, ammonia facilitates development. Ammonia does not act on the developable image as it does act on silver sub-bromide. This, therefore, is evidence that the developable image does not consist of silver sub-bromide.

"The author believes that all the facts known to bear on this subject agree with the supposition that the developable image consists of particles of silver salt, rendered less stable but not decomposed, and that no particle can be developed that has not been itself immediately affected by the exposure. It should be borne in mind, however, that light is not homogeneous, and that its effects vary according to its wave length. There may, therefore, be more than one change going on during the exposure of a gelatine-bromide plate. And it is possible that the nature of a developable image varies; it may be different on a gelatine dry plate from

what it is on a wet collodion plate, and again different when a daguerreotype plate is employed.

"All ideas as to the exact character of the change that occurs in the silver salt when light produces a developable image are exercises in imagination. It has been suggested that the silver bromide is ionized, that the molecular grouping in which perhaps it exists is modified, or that a kind of crystallization action takes place; but these and other ideas of the same sort do not serve to correlate the facts that are known, and their usefulness is not apparent.

"A working hypothesis that the author ventures to indicate in the crudest of terms for the sake of clearness views the silver bromide either in single molecules or molecular aggregates as if the silver and bromine were flat figures, say like two visiting cards arranged edge to edge in the same plane, as they would be laid upon a table side by side. The change of this group into a developable condition would consist in the rotation of one about the axis common to both until it was in a plane at right angles to the plane of the other, this rotation at the same time screwing the one away from the other. Such a system would evidently be less stable under certain conditions than the original. By the continued action of light the rotation would continue until the two parts were both again in the same plane, and this would represent reversal—an undevelopable condition produced by a continuance of the change that produces the developable condition. The further action of light producing further rotation, a second developable condition results, but less marked than the first, as the increased rotation has separated the two parts further from each other. As the rotation continues the developable and undevelopable condition alternate, but rapidly become confused until the two parts are really forced asunder and actual decomposition results. The student can for himself apply this suggestion to all the facts of the case."

Although Namias showed that stannous chloride will apparently produce a latent image on a dry plate, he does

not admit for a moment the accuracy of the sub-bromide hypothesis.[1]

"How does stannous chloride produce a latent impression? The advocates of the chemical hypothesis will find in these experiments of mine a new argument in favor of their view. They will certainly say that stannous chloride is a powerful reducing agent and that it therefore reduces silver bromide to sub-bromide. It is easy, however, to show that the amount of this reduction must be infinitely small. A plate, 9 cm × 12 cm, may be assumed to have at least 0.1 gram silver bromide in the film, and this plate will be completely changed by the prolonged action of 50 cc of a stannous chloride solution (1 : 200,000); in other words by the action of 0.00025 gram stannous chloride, assuming that all the stannous chloride in the solution enters into the reaction; unquestionably only a small portion of the total stannous chloride reacts. This amount of stannous chloride is only sufficient to reduce 0.0001 gram silver bromide to sub-bromide. At most, therefore, only one one-thousandth of the total amount can have been converted into sub-bromide.

"For ten years I have combatted the sub-bromide hypothesis on the basis of many experiments and this one serves to strengthen my theoretical views. Since so little sub-bromide is formed, one may well ask how the reduction of all the silver bromide is brought about.

"I will not go further with these theoretical considerations and I return to the experiments. If a plate or if silver bromide paper be dipped in a three percent stannous chloride solution and then dried, it will give an image by direct printing if exposed long enough to the light. The image is not dissolved by thiosulphate. In this way one can use plates and papers which would otherwise be worthless on account of fog and one can obtain pictures by a printing-out process. In no other way have I been able to obtain such sharp pictures with silver bromide without development.

[1] Namias: Phot. Correspondenz, 43, 155 (1905).

I have used oxalic acid and oxalates several years ago as sensitizers for silver bromide and they produce images fairly readily; but the image is dissolved almost completely by thiosulphate.

"The reduction by light in presence of oxalic acid is, therefore, not so thorough as in presence of stannous chloride. In the first case the action of light forms silver sub-bromide only and this substance dissolves to a great extent in thiosulphate. In the second case light must reduce the silver salt to metallic silver because thiosulphate scarcely attacks the image at all. The blackening of silver bromide by light takes place very rapidly when stannous chloride is present."

Namias has discussed the question of the latent image at some length in his book.[1]

"Without question one of the most marvelous things in photography is the formation of the latent image. The halide salts of silver—chloride, bromide, and iodide—are specially noticeable for the characteristic of changing in consequence of a very short exposure to light, thereby forming a latent image, the existence of which can only be shown by development. It is hard to say what change the silver salts undergo during a very short exposure to light. It is so slight in amount that it escapes our senses and all physical or chemical methods of investigation.

"To account for the formation of latent images, we have recourse to hypotheses, and these hypotheses are of two kinds. According to one point of view the action of light produces a real and definite chemical change. According to the other point of view we are dealing with a physical or molecular change. It is possible to make out a strong case for either point of view.

"The hypothesis that we are dealing with a chemical change is at first sight the most plausible one. We know that when silver chloride, bromide and iodide are exposed to light for a sufficient length of time, halogen is set free and

[1] Namias: Chimie Photographique, 102, 110 (1902).

they become black. There is produced a chemical decomposition which can be followed. The total amount of decomposition, increases as the exposure is increased. It, therefore, seems legitimate to assume that the decomposition which one can see when the action of light has been prolonged sufficiently, is the reaction which takes place to an infinitesimal degree when the exposure to light is very short and that it is this decomposition which gives use to the latent image.

"In support of this hypothesis is the fact that chlorine, bromine and iodine destroy the latent image when allowed to act on a plate which has been exposed to light. It looks as though this destruction of the latent image were due to a regeneration of the substance which had been decomposed by light.

"The upholders of the chemical theory claim that the very brief action of light causes the formation of a very small amount of sub-chloride, sub-bromide, or sub-iodide of silver. If AgCl, AgBr and AgI are the formulas of the chloride, bromide, and iodide of silver, respectively, the formulas of the corresponding sub-halides will be Ag_2Cl, Ag_2Br, Ag_2I. There is satisfactory evidence of the existence of these sub-salts and one may claim that the blackening, at least in the first stages of exposure, is due to the formation of sub-halides rather than to the precipitation of metallic silver. The amount of the sub-halides constituting the latent image is, however, very small. According to Eder the amount of bromine set free from a surface of ten square centimeters of a silver bromide gelatine emulsion cannot be more than a millionth of a gram. Since this amount of emulsion will contain at least 0.25 gram of silver bromide, it follows that the amount of sub-bromide formed according to the chemical hypothesis will only be a little more than a millionth [hundredth-thousandth?] of the silver bromide in the sensitive plate.[1]

"The fact that some substances which react readily with chlorine, bromine or iodine (chemical sensitizers) facili-

[1] [Eder gives the figure as one in a thousand. W. D. B.]

tate the formation of the latent image would seem to prove the chemical nature of the change produced by light. It is not easy to explain the action of these substances so long as one claims that the change is purely molecular and that none of the chlorine, bromine or iodine is eliminated.

"We have now given some of the evidence in favor of the chemical hypothesis. There are certainly as many and as good reasons for accepting the hypothesis that the invisible change produced by light is entirely physical or molecular. Let us consider the daguerreotype for a moment. The latent image is formed on a plate of silver covered with silver iodide, and it is developed by means of mercury vapor. The action of the mercury is purely physical, the mercury condensing on the places which have been exposed to light. Must we admit that a chemical change in silver iodide has taken place in order to account for its having acquired the property of retaining mechanically the vapor of mercury? Most certainly not.

"Moser's experiments have a bearing on this question. A coin was placed on a glass or a metal plate and left there for several hours. If one breathes on the plate where the coin had been, or passes the vapor of iodine or mercury over it, there is a differential condensation on the places which have been in contact with the coin and an image of the coin is thus formed. What appears more strange is that one can obtain an image and can develop it in this way, even without actual contact between the coin and the plate. It is enough if the coin is near the plate.

"These facts have nothing to do with the action of light, but light will produce similar phenomena. In fact, if one exposes a plate of silver, copper or glass to an intense light for several hours, one notices that water vapor from the breath or mercury vapor will *develop* the parts which have been exposed to the action of light.

"In the cases thus cited the change which makes it possible to develop parts of the glass or metal plate is purely a physical one. Why not, then, admit that with the daguerreo-

type plate the change, which makes it possible for the silver iodide to condense the mercury vapor, is also a purely physical one?

"If we admit this for the daguerreotype plates in which the light-sensitive material is silver iodide, why should we not also assume a purely physical phenomenon to account for the change taking place in other light-sensitive preparations of silver halides, even though the latent image is developed with a liquid instead of a vapor and by a chemical process instead of a physical one?"

"If we adopt the hypothesis of a physical modification, we may be asked how we account for the destructive action of chlorine, bromine, or iodine on the latent image. It is not easy to find a completely satisfactory answer to this; but if the destructive action of chlorine, bromine, or iodine is in keeping with the chemical hypothesis and confirms it, we cannot say the same for the action of other substances such as potassium iodide for instance. We do not know how to account for the action of potassium iodide on the sub-halide and yet we know that this salt destroys the latent image under some conditions.

"The spontaneous disappearance of the latent image, makes the acceptance of the chemical hypothesis very difficult; and this decay of the image is common to all negatives, though the time necessary varies with different plates. We know that with daguerreotype plates the latent image disappears in a very short time. This disappearance takes place quite independently of any external action. It is precisely in the daguerreotype process, that the latent image disappears rapidly even though this is the process in which a chemical explanation of the phenomenon is hardest to find. In order to account for the disappearance, it is not permissible to postulate that the sub-iodide, formed by the light, takes up iodine again. If we grant that a small amount of the iodine is set free by the light, it will react at once with the silver plate to form more silver iodide. It is hopeless to fall back on the action of substances in the sensitive film

because there is no silver nitrate nor any other substance which might decompose gradually and tend to reverse the action of light."

"The invisible change which moderate pressure produces upon the silver halides, must be a polymerization. All forms of energy produce the same effect when they act to a limited extent. The hypothesis, that the first action of different forms of energy on silver bromide causes a polymerization, gives us a plausible explanation for development by reduction. In development by reduction, which is the usual method for bromide dry plates, the latent image becomes visible because the halogen (chlorine, bromine, or iodine) is removed more rapidly from the portions exposed to the action of light (or of any other form of energy) than from the other portions. There is a setting free of silver which is the substance forming the visible image. If now we postulate for silver bromide two formulas, AgBr, and Ag_2Br_2, the second being a polymer of the first, it seems reasonable to assume that the silver bromide corresponding to the second formula is more readily decomposed in consequence of the atoms of silver being in some way partially connected in the molecule and also the atoms of bromine, so that the affinity between silver and bromine is diminished thereby, with the result that decomposition should apparently take place more readily.

"Let us now consider another phenomenon which furnishes another argument for the molecular or physical hypothesis. We know that the latent image on a silver bromide gelatine plate becomes, when developed, more dense at the points where action of light has been most intense. We know also that under normal conditions the image shows no tendency to spread sideways. If we claim that the invisible modification produced by light is a sub-bromide, we must admit that the chemical modification is limited to an infinitely small fraction of the sensitive film, because we have already seen that only an infinitesimal amount of silver sub-bromide is formed. It is, therefore, necessary to account

for the reduction of the silver bromide to metallic silver extending through the whole thickness of the film. To do this we must admit that a physical action plays an important part in the development and that, in consequence of an attraction between the silver (reduced from the sub-bromide) and the unchanged silver bromide, the image can develop to a greater depth. If we are going to speak of an attraction or of any other physical action, why should this action take place in different amounts at the points in the plate which have received different exposures, and why should the action make itself felt in the depths of the film and not at the side of the image?

"We believe that it is hopeless to search for a rational explanation of these facts if we assume the chemical hypothesis. We could also cite other facts which have had an influence in making us abandon this hypothesis.

"In an article published in *Archiv wiss. Photographie*, for 1899, Professor Abegg resuscitated the hypothesis that the formation of the latent image is due to the precipitation of an infinitesimally small quantity of metallic silver, which then acted as a nucleus and facilitated the reduction of the surrounding silver bromide. In confirmation of this hypothesis, Abegg established the fact that dilute nitric acid tends to destroy the latent image by reacting with the metallic silver. Before that, it had always been supposed that nitric acid did not have such an action and this was looked upon an an argument in favor of the sub-bromide hypothesis because this was supposed not to be attacked by nitric acid while metallic silver is attacked. Further, we know from Eder's experiment that, if an unexposed silver bromide gelatine plate is immersed in a developing bath and is brought in contact with a silver wire, reduction takes place at the point of contact. This proves that metallic silver really has the power of facilitating the reduction of silver bromide with which it may be in contact. In addition, an experiment by Abney supports this view. Abney showed that if a finished negative is placed in contact with an unexposed

emulsion and if the two are then placed in a developing bath, the image is re-enforced by reduction of the silver bromide in the superposed film. Another interesting fact, recently discovered, may be cited in support of Abegg's theory. If an exposed dry plate is fixed in a hyposulphite bath before it has been developed, and is then plunged into a silvering bath such as is used in the collodion process, an image appears. It is claimed that this happens because the hyposulphite has dissolved the unchanged silver bromide, leaving intact the infinitesimal quantity of silver set free by the light. This silver causes the deposit on itself of silver from the bath.

"In spite of the excellent reasons in support of this chemical theory, which is much superior to the one based on the assumption of the sub-bromide, it will not be accepted by everybody. Why should one admit that this infinitesimal quantity of metallic silver forms regularly throughout the whole depth of the film which is to be developed? Why does the silver reduced by light exert an attraction on the silver bromide to be reduced in the developing bath only downwards through the film and not sideways from the points which have been exposed to light? We might make many other objections but there is always the difficulty of accounting for the way in which development takes place, when we adopt any theory which presupposes an attraction. In order to be free from the objections just cited, any theory, molecular or chemical, must postulate that the change which makes the silver salt developable occurs in all the particles of silver salt exposed to light and not merely in a few of them.

"This is exactly what is postulated by our theory, which assumes a molecular change, which change may be a polymerization as we have pointed out, or may be something entirely different.

"The experiments, recently made by the Messrs Lumière as to the action of light on dry plates which had been cooled to a very low temperature (— 190°) by means of liquid air have shown that the rate of formation of the latent image is much decreased by a lowering of the temperature. To

produce the same image the time of exposure must be increased fifty to four hundredfold that necessary at ordinary temperature. This would be a reason for doubting that the change was a physical one, and for claiming that the change must be a chemical one because the chemical phenomena are the ones that are the most affected by temperature. These experiments do not however, tell against our hypothesis of a molecular change, because the temperature also has an effect on molecular modifications.

"The energy which produces the molecular change must not be considered as merely starting the reaction without being absorbed, but it must be considered as being absorbed and as actually doing work. Though this work may be small, it nevertheless decreases the total amount of work which would be necessary to decompose a silver salt which has not been exposed to light.

"The silver halides are very remarkable in that the equilibrium of their molecules may be disturbed by any form of energy. They are still more remarkable because the slight disturbance produced by the first action of light or of any other form of energy, changes the manner of reacting with certain substances in such a way that it becomes possible to replace the invisible image by one that can be seen."

Namias assumes that silver bromide is polymerized by light. On the other hand, Hurter and Driffield[1] believe that light depolymerizes the salt.

"The application of thermo-chemical data to the theory of development, having shown that the whole of the energy required for the decomposition of silver bromide may possibly be, and probably is, derived from the changes which the developer undergoes during development, it would appear to be possible to dismiss the old theory of the constitution of the latent image long held by many authors.

"The idea that some portion of the silver bromide is decomposed by the light into a sub-bromide and free bromine,

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[1] Phot. Jour., 22, 149 (1898).

is not necessary for the explanation of the phenomenon o development. It is quite sufficient to assume that the light causes some change in the molecular structure of silver bromide; that it changes, for instance, a complex molecule Ag_nBr_n into simple ones. We may assume that the light does some work of disgregation, as Clausius would say; not involving a complete change in chemical composition, such as the formation of a sub-bromide, but work, such as is done during the change in the crystalline structure of sulphur or of calcium carbonate; work which requires a much smaller amount of energy than the complete separation of atoms of bromine from the molecule of silver bromide would involve.

"There is absolutely no experimental proof that the change which silver bromide undergoes when exposed to light of such small intensity, and for such small periods of time, as suffice for the production of photographic negatives, produces any visible effect or any measurable chemical transformation. All that can be proved is that silver bromide is more rapidly attacked by the developer than unexposed silver bromide; but the character of the change (whatever its nature) and its progress in course of time are identical for the exposed and for the unexposed silver bromide.

"When silver bromide is treated with a solution of potassium iodide, chemical decomposition takes place, the bromine and iodine are exchanged, and we then have silver iodide. This reaction takes place also in the case of silver bromide in the sensitive film. If silver bromide which has been exposed to light (*i. e.*, impressed with a latent image) consisted of sub-bromide, this sub-bromide would either remain as such, when treated with potassium iodide, or it would yield a sub-bromide. In either case it ought to yield, upon development, a visible image; but the treatment of a latent image with potassium iodide completely destroys the image, and we must therefore conclude that the latent image consists of bromide of silver, possibly in an allotropic modification.

"If a film containing exposed silver bromide be treated with potassium bromide, no effect whatever is produced; the latent image can be developed in its full vigor after the potassium bromide has been washed out.

"Again, if a sensitive gelatino-bromide plate be treated with a dilute solution of bromine in water, the film loses its sensitiveness to light, that is, the plate becomes exceedingly slow. If the sensitive plate had a latent image impressed upon it by suitable exposure to light before it was treated with bromine, this latent image would no longer be capable of development; the difference in rapidity of attack by the developer on the exposed and unexposed silver bromide would have vanished.

"This peculiar behavior of the film under the influence of free bromine, shows that if the action of the light upon the sensitive film were continued so long as to bring about actual decomposition, and so produce a certain amount of free bromine the bromine thus liberated would efface the latent image, and render the film almost insensitive. This is exactly what happens when the exposure is continued so long as to produce the phenomenon of reversal.

"That any ordinary camera exposure is inadequate to produce a material decomposition of the silver bromide on the plate can be shown by other experiments and considerations. A standard candle consumes 120 grains or 7.77 grams of spermaceti per hour, or about 0.0021 gram per second. The energy evolved by the combustion of 0.0021 gram spermaceti (1 gram = 10000 units of heat) is 21 gram-units (small calories). If the whole of this energy were produced in the form of chemically active light and evenly distributed over a sphere of 1 meter radius = 125,663 square cm, the amount of energy per 100 square cm of surface would be $\frac{21 \times 100}{125,663} =$ 0.016 gram-units of heat.

"While it is possible on a sensitive plate to produce a deposit of 26.5 milligrams of metallic silver per 100 square cm area by an exposure of 10 C.M.S., the amount of energy

received by this area, assuming the whole energy yielded by the candle to be taken into consideration, as in the above calculation, is 10 × 0.016 = 0.16 units in 10 seconds. Now the decomposition of silver bromide, equivalent to 108 milligrams of silver, requires energy amounting to 23 gram-units and the energy necessary for 26.5 milligrams of silver is 5.6 units, so that the candle, even if the whole of its energy of combustion were active in decomposing silver bromide, could only decompose 2.9 percent of the amount which experiment shows can be actually rendered amenable to development. As a matter of fact, however, only a small fraction of the energy of the candle is transformed into radiant energy; and again, a very small fraction of the radiant energy constitutes ethereal waves of sufficiently short wave length to affect silver bromide. It is thus rendered quite evident that the candle can only furnish an infinitesimal part of the energy necessary to produce 26.5 milligrams of metallic silver per 100 square cm with an exposure of 10 C.M.S., and that the whole of this energy is, in all probability, provided by the developer.

"We have, moreover, furnished the proof, as far as this can be done, that the composition of the latent image is, as nearly as possible, AgBr; and in a paper, published in February, 1891, we showed that no bromine is liberated in the course of development. As this paper may not be readily accessible, we will briefly repeat our experiment therein recorded.

"A gelatino-bromide plate ($6^1/_2$ by $4^3/_4$ inches) was exposed to the light of two standard candles, one on either side of the plate at a distance of half a meter, for 33 minutes. The plate was then well washed with pure distilled water to remove any bromine which might either become free as such, or which might, by action on the gelatine, have formed hydrobromic acid. The result was that no soluble bromine could be detected in the wash water.

"The plate was then developed with ammoniacal pyrogallol for 30 minutes and washed. The developing solution

and the wash water were together oxidized with nitric acid and the bromide precipitated, washed, filtered, and weighed as metallic silver. The weight found was 197.7 milligrams.

"The plate was then fixed in pure thio-sulphate, well washed, and the film stripped. The amount of metallic silver contained in the film was determined and found to be 194.4 milligrams. The amount of bromine in the developer was thus slightly more than the equivalent of the metallic silver found in the developed plate. Hence we must conclude that the chemical composition of the latent image is AgBr; and this silver on the plate had been brought into a readily developable form.

"The behavior of exposed silver bromide to a solution of potassium iodide only furnishes qualitative results.

"The behavior of exposed silver bromide to a solution of potassium bromide is shown by the following experiments. A plate which had received a series of graduated exposures was cut into two parts. One part was soaked for 20 minutes in a solution of potassium bromide, and then washed for 40 minutes. The other part was soaked in water for 60 minutes. Both parts were then developed and gave the following result.

EXPERIMENT 1

Exposure C. M. S.	Density. Plate D_x	
	Soaked in KBr	Soaked in water
0.625	0.065	0.060
1.25	0.360	0.385
2.5	0.870	0.910
5	1.305	1.365
10	1.740	1.820
20	2.190	2.230
40	2.515	2.510

"That, in course of time, the rate of action of the developer upon unexposed silver bromide is the same as upon exposed, is shown by the following comparative results:

TABLE III

	Plate	Time of development		
		2 min.	4 min.	8 min.
Unexposed	D_9	0.745	1.165	1.765
Unexposed	D_6	0.760	1.370	2.140
Unexposed	D_2	0.790	1.290	1.890
Exposed 2.5 C. M. S.	G	0.660	1.095	1.600
Exposed 10 C. M. S.	H_2	0.505	1.200	1.965
Exposed 20 C. M. S.	D_7	0.650	1.270	1.945

"In the case of the unexposed plates, the developer contained no bromide, while bromide was used in the case of the exposed plates. It will be seen, however, that the growth of density with time is nearly the same in both cases.

When unexposed and exposed silver bromide are developed together, this equal rate of growth is not so easily detected since the action of the developer upon the unexposed silver bromide is then comparatively small, but the ratio does approximate to equality, as is shown by the following experiments, in which the exposed and the unexposed plates were developed together.

TABLE IV

Plate D_t developed	2 min.	4 min.	Ratio
Unexposed	0.175	0.300	1.71
Exposed 1.25 C. M. S.	0.370	0.615	1.66
Exposed 2.5 C. M. S.	0.725	1.100	1.51
Exposed 5 C. M. S.	1.040	1.520	1.46

"These experiments show that the difference between unexposed and exposed silver bromide is of the same character as the difference between two successive exposures; it is a difference of degree only, and not of kind.

"Our previous experiments and calculations indicate that it is highly probable that the difference in the amount of energy contained in the exposed and unexposed silver bromide is very small, and that the rapidity with which the

developer attacks the unexposed films of plates, varying conside ably in speed, is almost identical, showing that there is a trifling difference, if any, in the amount of energy contained in the unexposed silver bromide, whatever the speed of the plate. The rapidity of attack of unexposed silver bromide in plates varying in speed is shown in the following table:

TABLE V

	H and D speed	Plate	Density developed in		
			2 min.	4 min.	8 min.
Unexposed	24	D_2	0.790	1.290	1.390
Unexposed	95	D_6	0.760	1.370	2.140
Unexposed	83	D_5	0.745	1.165	1.765

"If, then, the silver bromide in rapid plates is of the same composition and contains the same amount of energy as that in slow plates, the difference in the speed of gelatino-bromide plates must be due more to their physical constitution and optical properties than to any difference in the silver bromide."

In commenting on this paper, Mr. Bothamley[1] said:

"One point, of which I was astonished to find that Messrs. Hurter and Driffield took no account in their paper, is the very great tendency of gelatine to combine with bromine. Mr. Driffield referred to a view held by various people to the effect that when light acts upon silver bromide there is formation of sub-bromide, and, as I thought he said, a setting free of the bromine; I can only say, in connection with that, that I do not know any chemist who has given attention to photographic questions and who holds any view of that kind. The evidence, as far as we have it at present, seems to me to be something like this: Gelatine is known to be capable of combining with great rapidity with large quantities of bromine. I have myself prepared these bromo-derivatives

[1] Phot. Jour., 22, 157 (1898).

of gelatine and it is quite easy to get solid compounds containing close upon 30 percent of bromine, and in the formation of these derivatives a very large amount of heat is developed. Now I will try to explain concisely the view which, as I understand it, is held by those who consider that a chemical change takes place in the production of the developable image. We know quite well, that in many cases, perfectly pure compounds show little tendency to undergo chemical change; for example, that combination will not take place between carbonic oxide and oxygen, if they are both quite dry. In the case under consideration, we have light as the active agent, and silver bromide as the substance that may undergo change. I am bound to admit, of course, that the evidence as to whether pure silver bromide alone is affected by light or not is rather vague, and the statement of different observers are rather contradictory; but there is an experiment of Schumann's which seems not to have attracted the attention it deserves. He covered one-half of a glass plate with gelatine, leaving the other half bare; then he put that plate in the bottom of a vessel in which he produced by precipitation some silver bromide, so that the precipitated silver bromide gradually settled down on the glass plate and come in contact with the glass of one-half and with the gelatine upon the other half. The plate was then lifted out, very carefully washed by gentle diffusion of water, dried, exposed to light, and treated with a developer; there was found to be practically no change in the silver bromide which had been in contact with the bare glass; but there was an abundant formation of reduced silver in the silver bromide that had been in contact with the gelatine. Therefore, in considering any question of the formation of the latent image, we must take into account the function of the gelatine. Everybody knows how different the phenomena are when silver bromide is in collodion and when it is in gelatine, and the view that I and others hold is that in a gelatino-bromide plate we have an intimate association of silver bromide and gelatine, and that when light falls upon the silver bromide it throws the molecules

of it into a violent agitation, and thereby, as Mr. Chapman Jones has already said, into unstable equilibrium. If the action of light is sufficient to produce a developable image it is because the condition of unstable equilibrium has reached such a point that part of the bromine, at least, ceases to be in chemical union with the silver and simultaneously combines with the gelatine; we do not believe that there is any setting free of the bromine in the ordinary sense of the term 'setting free.' Now, Messrs. Hurter and Driffield describe an experiment which they consider proves that the composition of the latent image is the same as that of the silver bromide, and the experiment consisted in treating a plate with a reducing agent and showing that there passed into the reducing agent or developer an amount of bromine equivalent to the amount of silver that had been reduced. Now what, I want to point out is that the experiment does not prove that all the bromine was in combination with the silver, because the reducing agent which would reduce the bromide of silver would most probably also reduce the bromo-gelatine; and it does not in any way disprove the view that I have endeavored to explain that silver sub-bromide and bromo-gelatine are formed, because the amount of bromine would be the same, and it would equally pass into the developer in the two cases. With regard to the statement that if you take an exposed gelatino-bromide plate, and treat it with potassium iodide, ycu destroy the latent image. Some few years ago, in preparing a paper on "The Latent Image," for a camera club conference, I treated two or three exposed gelatino-bromide plates, with a five percent solution of potassium iodide for a considerable time, washed out the potassium iodide, treated the plates with the developer, and casual observation would have led one to suppose that the developable image had been destroyed; some later work, however, threw doubts upon that conclusion; it seemed possible that the latent image was there, but that the time required for its development was very long, and I found that by allowing the ferrous oxalate developer to act for a good many hours

I was able to develop an image. Recently, Schumann has made an experiment in which he has found that the ordinary belief that an emulsion of silver iodide in gelatine will not give a latent or developable image is contrary to actual fact, and that if such an emulsion is subjected to light of very high refrangibility you can get an image and develop it just as in the case of silver bromide. Therefore, coupling these facts with the well-known fact that there are certain chemical reagents which will cause the disappearance of the developable image, while other chemical reagents will not, I am bound to-day that, while I do not commit myself to any definite opinion as to the precise composition of the image, it seems to me that the evidence in favor of some chemical change is very considerable, and certainly that the experiment of measuring the amount of bromine that goes into the developer does not prove anything to the contrary."

To this, Messrs. Hurter and Driffield[1] replied:

"Professor Bothamley has directed most of his remarks to chemical changes, which he believes to be induced by the light, and which he supposes to be so profound as to actually reduce the silver bromide to some sub-bromide. Whatever may be the formula of this sub-bromide, it means the complete separation of some bromine from silver. Professor Bothamley does not say that the energy necessary for this reaction is supplied, even in part, by the supposed formation of a bromine compound of gelatine, but this must be the meaning of his remarks as to the facility of the formation of a bromine compound of gelatine and as to the amount of heat developed. His belief summed up appears to be that the latent image is formed by the transference (under the influence of light) of bromine from the silver bromide to the gelatine, with the consequent formation of some sub-bromide of silver, the possible existence of which, as a laboratory product, we do not deny. But we have always understood these sub-bromides to be colored bodies, and the latent

[1] Phot. Jour., 22, 151 (1898).

image resulting from ordinary photographic exposures is not colored. Professor Bothamley will readily admit that bromine when combining with gelatine will do so either by forming a substitution product (when hydrobromic acid will appear as well) or by forming a simple addition product. Our quantitative experiments are quite decisive as to the non-production of hydrobromic acid, and to prove that there is, at any rate, no substitution product. They are, however, not decisive as regards the formation of an addition product, and this fact was stated in our original communication in 1890.

"But whichever product be formed, the great question still remains—whence is the energy derived which separates the bromine from the silver? The possible formation of a bromine compound of gelatine may reduce the amount of energy required to bring about this separation to about one-half of the 23 calories, since the heat involved on substituting bromine for hydrogen is, at most, 11 calories per atom of bromine taken from the silver; and 14 calories if an addition product be formed. The greatest difficulty with regard to the sub-bromide theory, therefore, still remains, namely, the energy difficulty; and it remains even if the combination of bromine with gelatine were a proved fact, which, as far as we are aware, it is not; it is simply an opinion."

Bredig[1] suggests that light may disintegrate the grains of silver bromide physically. The disintegrated particles would have a higher solubility than the others owing to the decrease in size. It seems reasonable to postulate that they would also be reduced more rapidly by the developer. Bredig is careful to point out that, although this hypothesis apparently describes the facts, it is quite possible that others may be equally satisfactory.

So far as I can understand Colson's rather vague account, he seems to think that gelatine is thrown into a state of molecular thrills by light quite as much as the silver bromide.[2]

[1] Eder's Jahrbuch der Photographie, 13, 365 (1899).

[2] Colson: La Plaque photographique, 19 (1897).

"It has thus been proved that the reaction of the hydrogen of the gelatine with oxygen or with chlorine retards the development of the latent image on a bromide gelatine plate. The part played by the organic matter is therefore very important. This throws new light on the formation of the latent image and on the way that the developer acts. Let us consider the action of any form of energy on the bromide gelatine plate. The impression is not visible but can be made so by development. The absorbed energy has then done a certain amount of work in the film, has started a change which will be completed by the developer. It is preliminary molecular work which precedes the decomposition. By increasing the vibratory movement of the molecules, it makes it possible for part of the hydrogen of the gelatine to come out and react with the substances for which it has a great affinity, oxygen, chlorine, bromine and iodine.

"We usually explain the action of the developer by saying that it reacts with the oxygen of the water, while the hydrogen thus set free reacts with the bromine of the bromide which has been made ready for decomposition by the light. We say that organic matter acts merely as an inert support. Since it does not react, by definition, no further attention is paid to it.

"The facts, which I have brought out, lead us to a more complete explanation. The oxidation of the developer, at the expense of the oxygen of the water in contact with the molecules of gelatine and bromide, causes an evolution of energy. This finishes the work started in the silver salt and the organic matter by light or any other form of energy. It makes the hydrogen of the gelatine combine directly with the bromine of the bromide or with the oxygen of the water thus setting free more hydrogen which may react with the exposed bromide.

"The mechanism is a direct and logical consequence of the great principle of the transformation and conservation of energy:

1. Increased excitation of the molecular movement

of the gelatine and bromide by luminous, calorific or thermal energy. This gives rise to the latent image which lasts for a certain time. We shall see other instances of this in phosphorescence, in the old experiments of Niepce de Saint-Victor, etc.

2. Another increase of the molecular movement of the gelatine and bromide by the energy set free during the oxidation of the developer. This evolution of energy, produced by oxidation, is increased, as we call it, by what we call an evolution of heat. This stimulus causes the separation of the molecules of hydrogen in the gelatine and of the molecules of bromine in the bromide. At the same time it makes the bromine combine with the hydrogen coming from the decomposition of water by the developer, and with the hydrogen coming from the gelatine.

"I lay stress on this new way of regarding the action of the developer because the whole of photography rests on the action of the developer.

"I call attention also to the fact that this theory, which follows quite naturally from the conception of molecular movement, is in itself sufficient without having to invoke what is called the chemical theory of the latent image, according to which it is assumed that the first action of light always produces a sub-bromide. This hypothesis is not only not necessary but it is contradicted by many facts. For instance, there is absolutely no color to the latent image when exposure is normal. A gray tint begins to appear only when the normal exposure has been exceeded. By that time there has been a reduction of bromide to sub-bromide; but, under these conditions, the developer gives rise to a reversed image, to a positive instead of a negative. The moment when the direct action of light causes a visible image is the moment when the developer begins to produce a reversal. This is the phenomenon of solarization."

Sheppard and Mees[1] have the following to say in regard to explanations of this type.

[1] Investigations on the Theory of the Photographic Process, 201 (1907).

"Analogy with elastic phenomena has suggested to many observers the idea of a 'strain' in the halide. In particular, J. C. Bose[1] has brought forward a 'molecular strain' hypothesis in explanation of the changes of conductivity, e.m.f., and surface tension of surfaces exposed to stimulus—mechanical stress or pressure, light, Hertzian waves, etc. It is maintained with regard to the photographic process that it gives a simple explanation of various obscure phenomena of the photographic action, such as the relapse of the latent image, recurrent and abnormal reversals, and dependence of the photo-effect on the time rate of illumination.

"This is not the place to criticize in detail Professor Bose's theory of 'molecular strain' in its applications to coherer action, response to stimulus, etc., but, as bearing on photography, we may suggest that there is a suspicion of a vicious circle in the argument. The elastic behavior of matter in bulk is transferred to the molecules, whereas a consistent molecular theory should surely afford an explanation of elastic phenomena themselves. Generally it may be said of the physical theories that they shirk a real explanation by treating the phenomenon to be explained as a quality of the physical modification of the halide, much as the narcotic powder of opium was attributed by mediaeval mediciners to a 'somniferous principle' peculiar to the drug. Meantime the primary fact requiring explanation seems to be somewhat neglected—namely, the acceleration of reduction by the developer."

In the next paper of the series, I shall discuss the hypothesis of the silver nucleus and the hypothesis of the silver sub-bromide.

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[1] Proc. Roy. Soc., 1902; Phot. Jour., 26, 146 (1902).

THE FUNCTION OF THE WALLS IN CAPILLARY PHENOMENA

S. L. BIGELOW AND F. W. HUNTER

The purpose of this investigation was to determine whether the material of which a capillary tube is made has any effect upon the height to which a liquid will ascend in it. The literature upon capillarity, which is extensive, does not furnish the desired information. G. Quincke[1] believed that water rose to different heights in tubes of different kinds of glass. P. Volkmann[2] subjected this conclusion to an exceedingly careful investigation and decided that the nature of the glass made no difference. Inferences may be drawn from the measurement of flat drops on different surfaces, but direct measurements of capillary ascension in tubes other than glass do not appear to have been attempted, probably on account of the fairly obvious difficulty arising from the fact that such tubes are not transparent.

It occurred to one of us that such measurements could, however, be made with great facility by applying a simple, well-known principle. The height of a column of liquid in a capillary tube is determined by the radius of the tube *at the meniscus*, and the size or shape of the tube below the meniscus makes no difference. Accordingly, if a tube of any convenient radius, say 3 mm be closed at the top by a thin plate of any material, through which a small hole is bored; if the whole be immersed in a liquid, and then gradually raised; a meniscus should form in this small hole, and the whole tube should remain full of liquid, until the height of the column is equal to that which would have been obtained with a long enough tube of the material of the plate, and of uniform bore the same size as the hole. When this point is reached, the meniscus should break away from the lower surface of the

[1] Wied. Ann., 52, 1 (1894).
[2] Ibid., 53, 633 (1894).

plate and the tube should empty. We found the facts agreed with this simple deduction in the most gratifying manner.

Apparatus

A cross section of the essential part of the apparatus we constructed for measuring capillary ascensions is shown on an enlarged scale in Fig. 1. The complete arrangement is shown on a diminished scale in Fig. 2 with the plate removed and as it appears while a height is being determined. A is the plate with the small capillary hole in it, resting on the glass tube B. This is carried by an arm C, which is raised or lowered by a ratchet and pinion mechanism such as is used for the coarse focussing adjustment on microscopes. Thus the tube and plate may be lowered until entirely submerged in the liquid in the beaker, and then it may be raised until the meniscus at the small hole breaks and the tube empties. At first we cemented the plates to the tubes, but cements dissolve and the solutions having different surface tensions are apt to produce irregular results. We discarded cements, put a rubber stopper on the tube and laid our plates on that. Only then did we realize that a further application of the principle on which we are basing our whole method made rubber as superfluous as cements. Suppose there is a crack between the plate and the top of the tube. It will fill with the liquid by virtue of the capillary forces, and will stay full and will not "leak" unless its width is equal to, or greater than, the radius of the hole in the plate. It is a very easy matter to grind off the top of the tube and to use flat plates so that the break, when it comes, comes always at the hole. We, therefore, merely laid the plates on the tubes and proceeded to make our observations. This simplification may appear trifling, but it is not, in fact, for three reasons. First, it much diminishes the time required to prepare for an experiment; second, it makes it much easier to clean the plates between experiments; third, it enables us to avoid substances which might contaminate our liquids or their surfaces.

After the liquid had fallen, we removed the plate, brought the point D to the surface of the liquid in the beaker, utilizing

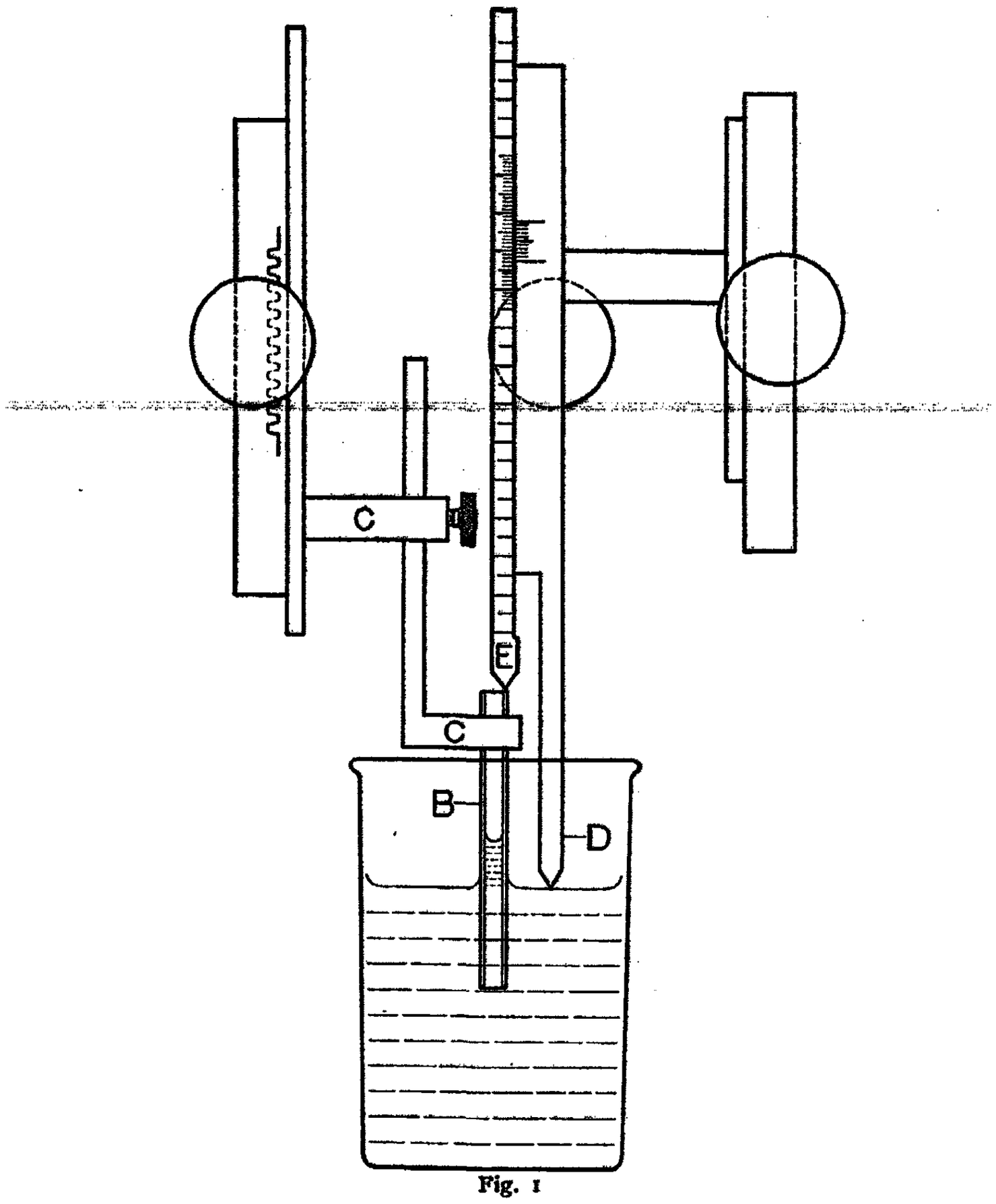

Fig. 1

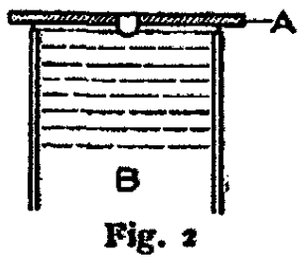

Fig. 2

the reflection of the point on the surface in the usual manner, and then brought the point E onto the edge of the glass tube. These points are carried by extensions independently movable, on one of which extensions is a scale in millimeters, on the other a vernier. We thus read the height to one-tenth of a millimeter, the limit of accuracy of our present instrument. We have in mind the construction of another with a micrometer screw to measure to 0.01 mm.

Two corrections must be applied to the height thus measured. First, the liquid falling out of the tube raises the level of the liquid in the beaker. From the diameters of the beaker and the tube and the height of the column, this correction is easily calculated. We found it more expeditious in most cases, however, to make a preliminary experiment to determine about the height to expect. We then repeated more carefully, and, after having raised the plate to within two millimeters of the breaking point, set the point D, then raised gradually till the break came, removed the plate and set the second point E. The second correction is as follows: the meniscus in the plate remains near the top at first, but when a height is reached within the thickness of the plate of the maximum height, the meniscus descends until it hangs by the lower edge, as indicated in Fig. 1. We assumed, for obvious reasons, that just before breaking it was hemispherical, with a radius equal to that of the hole. We, therefore, subtracted this radius from the measured height. It would have been more accurate had we subtracted 2/3 of the radius, but this refinement falls at the limits of our experimental errors.

It should be mentioned that we lay no particular stress on this ratchet and vernier instrument, and recognize that a cathetometer telescope would have certain advantages. It would take longer to make the readings with the telescope, but they would be somewhat more accurate.

For drilling the holes in the plates, we used a jeweller's lathe and drills, holding the drill stationary and revolving the work. We examined the holes and measured them

with a good microscope, a stage micrometer and micrometer ocular. We had the customary difficulties in our efforts to secure strictly round holes. None of them were round within the limits of our measuring instruments, but they were as nearly round as the bores of the tubes used by previous investigators of capillary phenomena.

Our measurements of the diameters of the holes were within 2 microns of right. On each hole we measured 10 to 12 diameters and took the average. The difference between the maximum and minimum diameters on one hole was never less than 5 microns. If this difference exceeded 20 microns, we did not use the plate. With the very thinnest metal plates and with salt plates, we were obliged to content ourselves with somewhat less regular holes. With some salts the deviation equalled 8 percent of the smallest diameter. Not infrequently, when we thought we had prepared a useful plate, we observed differences between maximum and minimum diameters as large as 60 microns. The holes in the plates were inspected and measured under the microscope before and after each group of observations, and if measurable differences were observed that group of observations was discarded. This was an absolutely necessary precaution in our work with soluble salt plates, and a reasonable precaution in our work with such metals as zinc and copper, owing to our method of cleaning.

Metal plates were washed by immersion in dilute sulphuric acid (1 : 3) for from 30 to 60 seconds, then transferred to distilled water, dried with filter paper and then dried at a distance of 20 cm above a bunsen flame. They were then washed in benzene, dried with filter paper and then again at the same distance above a bunsen flame. The salt plates were merely dried as rapidly as possible with filter paper after removal from the solution.

We secured the desired temperature and held it constant within 0.5° by standing the beaker in a large shallow jar of water to which we added hot or cold water as needed.

After having developed the method as described above,

we discovered that Oersted[1] had devised a similar apparatus based on the same principle, in 1841. In Oersted's apparatus, one arm of a U tube carried a plate with a hole in it. A side arm enabled him to alter the level of the liquid in the other arm of the U tube. He raised the level here till liquid was forced out through the capillary and measured with a cathetometer the liquid pressure required. He also lowered the level in the other arm until the meniscus broke away, as in our work. This is a less convenient application of the principle than ours and less free from possible errors. He determined that an amalgamated copper tube and a glass capillary tube raise water to the same height. He also determined the capillary ascension of mercury in an amalgamated copper tube and that is all. The article is but three pages long. He expresses his intention of continuing this line of investigation, but we have not found anything further by him. He died in 1844. It is indeed strange that no one else appears to have utilized his apparatus.

Results

Although we felt reasonably certain that the thickness of our plates could make no difference, we carried out a set of experiments to prove the fact. Our results are contained in Table I. This, and the succeeding tables containing our results, are self explanatory, and require but few remarks. All measurements are expressed in millimeters. The first column contains the thickness of the plates, the second the radius of the capillary hole in the plate, the third, the highest ascension obtained, the fourth, the lowest, the fifth, the number of separate observations, the sixth, the average, and the seventh, the product of this average into the radius. The values in the seventh column should then be constant. Each horizontal line represents an entirely separate group of experiments, in many, if not most instances, carried out on different days. A microscopical inspection of the hole preceded and followed each of these groups.

[1] J. C. Oersted: Pogg. Ann., 53, 614–16 (1841).

Our glass plates were sections cut off a capillary tube and ground down to the given thickness with fine carborundum and a solution of camphor in turpentine.

TABLE 1

Copper Plates—Water. Temp. 20.5–21°

Thickness of plate	Radius of hole	Highest	Lowest	No. of readings	Average	hr.
0.07	0.316	47.9	47.3	3	47.61	15.04
0.14	0.250	60.3	59.3	4	60.11	15.03
0.15	0.243	62.3	62.3	2	62.31	15.15
0.10	0.243	62.8	61.5	4	62.31	15.15
0.20	0.296	51.1	50.8	4	50.95	15.08
0.68	0.289	52.1	52.0	4	52.10	15.05
0.81	0.293	51.9	51.2	5	51.72	15.16
0.83	0.285	53.8	53.8	2	53.78	15.32
1.13	0.240	62.7	62.6	3	62.70	15.05
					Av.	15.115

TABLE 2

Platinum Plates—Water. Temp. 20.5–21°

0.08	0.283	52.3	51.7	5	52.15	14.76
0.08	0.269	54.6	54.4	4	54.58	14.69
0.08	0.314	47.2	46.4	5	46.83	14.70
					Av.	14.72

TABLE 3

Zinc plates—Water. Temp. 20.5–21°

0.24	0.304	50.5	50.0	5	50.24	15.27
0.24	0.306	49.3	49.1	3	49.15	15.04
0.24	0.293	51.2	51.1	4	51.14	14.98
0.24	0.271	56.0	55.6	5	55.81	15.12
0.24	0.308	49.5	49.2	5	49.25	15.17
0.24	0.309	49.5	48.9	5	49.19	15.20
0.24	0.306	50.1	49.7	4	49.93	15.28
					Av.	15.15

TABLE 4

Nickel Plates—Water. Temp. 20.5–21°

Thickness of plate	Radius of hole	Highest	Lowest	No. of readings	Average	hr.
0.53	0.304	49.4	49.3	3	49.37	15.01
0.53	0.299	50.0	49.5	5	49.81	14.89
0.53	0.306	49.2	48.5	5	48.90	14.96
0.53	0.274	55.2	54.6	5	54.74	15.00
0.53	0.269	56.2	55.4	5	55.70	14.98
0.53	0.305	49.8	49.0	5	49.34	15.05
0.53	0.275	55.2	54.9	4	54.99	15.12
					Av.	15.00

TABLE 5

Silver Plates—Water. Temp. 20.5–21°

Thickness of plate	Radius of hole	Highest	Lowest	No. of exps.	Average	hr.
0.28	0.261	56.2	55.6	4	55.98	14.61
0.28	0.260	57.3	57.0	5	57.26	14.89
0.28	0.258	57.3	57.1	5	57.18	14.75
					Av.	14.75

TABLE 6

Aluminium Plates—Water. Temp. 20.5–21°

0.87	0.301	49.2	48.6	4	49.00	14.75
0.87	0.298	49.3	48.7	3	49.10	14.63
0.87	0.299	49.6	49.0	6	49.30	14.74
0.87	0.312	47.8	47.0	7	47.50	14.82
0.87	0.302	49.6	49.2	5	49.43	14.93
0.87	0.306	49.8	48.6	6	49.16	15.04
0.85	0.295	50.5	49.3	6	49.69	14.66
0.86	0.299	49.3	48.7	3	49.07	14.68
					Av.	14.78

TABLE 7

Glass Plates—Water. Temp. 20.5–21°

1.87	0.312	47.2	46.8	4	47.04	14.68
1.90	0.312	47.2	47.1	3	47.15	14.71
					Av.	14.69

TABLE 8

Celluloid Plates—Water. Temp. 20.5–21°.

Thickness of plate	Radius of hole	Highest	Lowest	No. of exps.	Average	hr.
0.75	0.243	58.3	57.7	4	57.91	14.07
0.75	0.233	61.5	60.9	5	61.30	14.29
0.75	0.236	61.6	59.1	7	60.04	14.17
0.75	0.236	60.3	58.0	7	59.21	13.97
					Av.	14.12

TABLE 9

Beeswax Plates—Water. Temp. 20.5–21°

1.70	0.340	38.8	38.3	5	38.48	13.08
1.15	0.315	42.3	40.3	10	41.45	13.05
1.50	0.316	41.4	40.9	6	41.08	12.98
1.65	0.310	42.1	41.4	5	41.92	12.99
					Av.	13.02

TABLE 10

Paraffin Plates—Water. Temp. 20.5–21°

2.5	0.258	37.5	36.5	5	37.10	9.57
2.0	0.305	31.5	30.1	6	30.91	9.43
1.8	0.268	37.2	36.4	5	36.87	9.88
1.8	0.272	36.4	36.4	1	36.4	9.90
					Av.	9.69

In Table 11, we have condensed the results given in detail in Tables 1-10, and have entered the substances in the order of the average values for rh obtained with them. This order is strikingly similar to that of the electromotive series of the metals. Aluminium falls out of place, doubtless owing to a protective coating of oxide upon it. We have included the highest and the lowest value for each substance to make it perfectly clear that our results overlap. Though the values for the different metals are not far apart, yet the lowest value for zinc is larger than the highest value for silver, and the highest value for glass is less than the lowest for nickel, etc.

TABLE 11

Plates of different substances. Temperature 20.5°–21°

rh values for water

	High	Low	Average
Zinc	15.28	14.98	15.15
Copper	15.32	15.03	15.11
Nickel	15.12	14.89	15.00
Aluminium	15.04	14.63	14.78
Silver	14.89	14.61	14.75
Platinum	14.76	14.69	14.72
Glass	14.71	14.68	14.69
Celluloid	14.29	13.97	14.12
Beeswax	13.08	12.98	13.02
Paraffin	9.90	9.43	9.69

It both surprised and interested us to find that with substances commonly spoken of as "not wetted," namely, with celluloid, beeswax and paraffin, we could not only get ascensions, but high and regular ascensions. Our results with these substances agree with each other as well as the results with plates of other materials, as may be seen by reference to Tables 8, 9 and 10.

We believe that our results are numerous enough, and have been obtained with sufficient care, to justify the statement that *water rises to different heights in capillary tubes of different materials.* This is a somewhat more pregnant statement than it might at first appear to be. The surface tensions, (γ), of liquids are frequently calculated from measurements of capillary ascensions, employing the well-known formulae $\gamma = \frac{rhs}{2}$, (s = specific gravity), when the angle of contact between liquid and wall is o, and $\gamma = \frac{rhs}{2\cos\theta}$ when that contact angle (θ) is greater than o. A polemic arose between Volkmann,[1] who maintained that the contact angle

[1] P. Volkmann: Wied. Ann., 17, 353–90 (1882); 53, 633–66 (1894); 56, 457–91 (1895); 62, 507–17 (1897).

between clean water and clean glass was o, and Quincke,[1] who maintained that under certain circumstances this angle had a measurable value.

Volkmann, employing many precautions in his experiments, obtained the value, $\gamma = 7.40$ for the surface tension of water at 20°. We claim no such high degree of accuracy as Volkmann's, for our separate results, yet our average for water and glass (see Table 7) was 14.69, and half this, or 7.35 would then be the value of γ; a satisfactory agreement. Now if that is the value for the surface tension of water at 20°, what are we measuring when we obtain our higher values with practically all the metals we have tried, and when we obtain our lower values with celluloid, beeswax and paraffin? The surface tension of one liquid at one temperature must be a constant, and since we obtain different values, it cannot be surface tension which we are measuring. It is possible that the contact angle between water and glass is not o, and that this angle is more nearly o between water and those substances with which we obtained higher ascensions. This view is the more probable as other methods for measuring the surface tension of water, the drop method, the bubble method, the ripple method, all give somewhat higher values than those obtained from the ascensions of water in glass capillary tubes. But one has not much more than stated the problem when he has demonstrated that the angle is o in some cases and greater than o in others. What interests us is, *why* is the angle different in different cases, or as we prefer to state it, why is the ascension of a given liquid different in tubes of different materials? This is a field in which but little, if any, direct experimental evidence has thus far been obtained, owing to the lack of a convenient experimental method.

A liquid rises and is held at a definite height in a capillary tube through the action of two forces, first, the cohesion between the like particles of the liquid which, in the surface layer is denoted by the phrase "surface tension" and second,

[1] G. Quincke: Wied. Ann., 2, 145–94 (1877); 27, 219–28 (1886); 52, 1–22 (1894); 61, 267–80 (1897).

the adhesion between the liquid and the walls. The arrangement may be likened to a chain with two links, and when such a chain is strained to the breaking point it is the weaker link which gives way. So, here, whichever is the weaker, adhesion, or cohesion must break first. The cohesion of a given liquid at one temperature must be considered as constant, not varying. We find the phenomenon of "breaking" at different strains, therefore we must be measuring the force of adhesion. The force of cohesion must be greater in all our experiments, except those giving the highest results, and in those cases we have no sure means of knowing which of the two forces it is which gives way. Because of these considerations, we have intentionally avoided the use of the conventional values for γ and have expressed our results in terms of the product of the radius into the height into the specific gravity, which is a measure of weight held up, and leaves open the question as to what relation these values bear to surface tension. For the above reasons, we call these values of ours adhesion values.

We wished to determine whether the capillary ascensions of other liquids than water were different with tubes (plates) of different materials. Tables 12–17 give the detailed results with benzene of specific gravity (s) 0.879 at 20.5°. Table 18 summarizes the results. It will be observed that the capillary ascensions show differences greater than can be attributed to experimental errors, and furthermore, that the order in which the substances fall is practically the same as with water, with the exception that silver and copper have changed places.

TABLE 12

Benzene Sp. gr. 0.879. Temp. 20.5° ± 0°.2

Glass plates h in mm

No. of plate	Thickness of plate	Radius of hole	Highest	Lowest	No. of readings	Average	hr.	hrs.
1	1.87	0.312	21.6	21.4	5	21.48	6.70	
2	1.90	0.312	21.2	21.1	4	21.16	6.60	
3	2.77	0.312	21.6	21.5	4	21.54	6.72	
						Av.	6.675	5.866

TABLE 13

Benzene Sp. gr. 0.879. Temp. 20.5° ± 0°.2

Platinum plates h in mm

No. of plate	Thickness of plate	Radius of hole	Highest	Lowest	No. of readings	Average	hr.	hrs.
3	0.08	0.283	24.2	23.9	5	24.15	6.83	
4	0.08	0.269	25.6	25.2	5	25.41	6.86	
5	0.08	0.314	21.8	21.6	5	21.72	6.82	
						Av.	6.839	6.012

TABLE 14

Aluminium plates

2	0.87	0.298	23.2	22.7	4	23.05	6.87	
3	0.87	0.299	23.1	22.9	5	23.08	6.90	
4	0.87	0.312	22.4	22.0	5	22.29	6.96	
						Av.	6.909	6.073

TABLE 15

Copper plates

3	0.15	0.248	27.6	27.4	5	27.54	6.83	
5	0.20	0.302	22.9	22.7	5	22.82	6.89	
6	0.68	0.290	23.7	23.4	5	23.57	6.84	
						Av.	6.852	6.023

TABLE 16

Nickel plates

A.B.	0.53	0.333	20.9	20.7	4	20.81	6.93	
A.A.	0.53	0.333	20.9	20.8	5	20.88	6.95	
A.C.	0.53	0.336	20.9	20.5	6	20.76	6.98	
						Av.	6.953	6.112

TABLE 17

Silver plates

1	0.28	0.261	27.6	27.5	4	27.53	7.18	
2	0.28	0.260	27.7	27.6	5	27.62	7.18	
3	0.28	0.258	27.1	26.6	5	26.82	6.92	
K.1.	0.29	0.352	19.9	19.5	5	19.64	6.91	
K.2	0.30	0.315	21.9	21.5	5	21.81	6.87	
						Av.	7.014	6.165

TABLE 18

rhs values for benzene. Temp. 20.5° ± 0.2°

Silver	6.16
Nickel	6.11
Aluminium	6.07
Copper	6.02
Platinum	6.01
Glass	5.87

We next undertook to determine the capillary ascensions of saturated water solutions of several salts in tubes of the solid solute. We obtained fair-sized plates by grinding down crystals, without reference to the position of the crystal axes. We felt that regard for the axes was a refinement which might advantageously be postponed until we knew more of what to expect in this new field. We saturated our solutions at higher temperatures and then cooled them to the temperature of the experiment, always having a considrable excess of the solid present in the beaker. We determined the specific gravities with a pycnometer at the temperature of the experiment in the usual manner. Otherwise, our procedure was in every particular as already described. We have results obtained with saturated solutions of copper sulphate, gypsum, common salt (halite), potassium dichromate and alum, and plates of platinum and of the solute. Upon repeating the work we have, however, obtained different values and deem it expedient to withhold these results until we can determine the cause of the discrepancy.

Conclusion

We have described a new and convenient method for determining the capillary ascension of liquids in "tubes" of any substance.

We have demonstrated that the capillary ascension of water (and of benzene) is different in tubes of different substances.

We consider it probable that the capillary ascension of liquids is primarily a measure of the adhesion between the liquid and the substance of the wall.

University of Michigan,
January 9, 1911

THE DIELECTRIC CONSTANTS OF SOME LIQUID HYDRIDES

BY R. C. PALMER AND HERMAN SCHLUNDT

Measurements of the dielectric capacity of liquid hydrides have been extended,[1] and values are reported here for the dielectric constants of liquid phosphine and stibine, and liquid and solid ammonia.

The dielectric constant of liquid ammonia was determined independently in 1899 by Goodwin and Thompson,[2] and Coolidge,[3] but we have found no record of a value for solid ammonia. As the dielectric constant of the solid was found to be much lower than that of the liquid, and the value of the liquid increases with lowering of temperature, a maximum value must intervene. Like many other substances the change in dielectric capacity of ammonia is abrupt and occurs at the melting point. The maximum value of the liquid, at —77°, was determined.

We were restricted, in our experiments, to the use of solid carbon dioxide and ether under diminished pressure for obtaining low temperatures. We found the preparation and liquefaction of ammonia and phosphine relatively easy operations in comparison with stibine. Since the boiling point of liquid stibine is only —18°, and its melting point, —91.5°, lies above the temperature of the cooling bath used, it seemed rather strange at first to meet with failures in securing the required quantities of this liquid. Beautiful mirrors of antimony appeared upon the walls of the connecting tubes, but only a few drops of liquid would accumulate in the condenser. Evidently the large volume of hydrogen generated simultaneously swept the stibine through the small U tube condenser too rapidly. By modifying the generator and using a tiny

[1] Cf. Schaefer and Schlundt: Jour. Phys. Chem., 13, 669 (1909).
[2] Phys. Rev., 8, 38 (1899).
[3] Wied. Ann., 69, 125 (1899).

spiral condenser the desired quantity of liquid stibine was ultimately obtained.

The measurements were made with the well-known apparatus of Drude as modified by Schmidt.[1] As the hydrides in question are gases at ordinary temperatures and atmospheric pressure, the measurements were conducted with the liquids in sealed cells. The U form of cell previously used[2] answered very well here. The cells were calibrated with the standard solutions of benzene and acetone, and acetone and water as given by Drude.[3] At least two independent determinations were made with different samples of each of the liquids and in cells whose dielectric capacity differed somewhat. The cells were recalibrated for each determination with freshly prepared samples of the solutions used as standards. The length of the stationary electric waves produced by the apparatus in air was determined and found to be 71.5 cm.

Preparation of Compounds.—In preparing the hydrides stress was laid on securing pure samples in the liquid state. After the different parts of the apparatus,—generator, drying trains, condenser, measuring cells, manometers, etc., had been sealed together, dry air was passed through the apparatus for an hour or two, and finally the apparatus was exhausted with a Geryk pump. The chemical action was then started and the gas condensed in a small condenser surrounded by Thilorier's mixture which could be kept under greatly reduced pressure if desired. The final measurements were conducted with samples that had been redistilled *in vacuo*.

The ammonia used in these experiments was prepared by allowing a concentrated solution of potassium hydroxide to drop upon a quantity of ammonium chloride in a suitable generator. The gas was dried in the usual way, and after condensation the liquid was distilled into the calibrated measuring cells, which had been previously sealed to the condenser. The cells were finally sealed off and transferred to the Drude

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[1] Drude's Ann., 9, 919 (1902).
[2] Jour. Phys. Chem., 13, 671 (1909).
[3] Zeit. phys. Chem., 23, 270 (1899).

apparatus where several sets of readings were made with each sample at several temperatures.

The samples of liquid phosphine used were free from the hydride, P_2H_4. Two of the specimens were prepared by the interaction of potassium hydroxide solution and phosphonium iodide, and a third was obtained by the interaction of aluminium phosphide and water as given by Matignon.[1] The gaseous phosphine was dried by passing through towers containing phosphorus pentoxide, after passing through a cooling condenser to remove traces of P_2H_4. The liquid phosphine was finally transferred to the cells by distillation *in vacuo*. With the exception of the rubber stopper of the generator all connections were glass seals.[2]

The samples of pure liquid stibine used were prepared by the method of Stock and Doht,[3] as later improved by Stock and Guttman.[4] An alloy consisting of one part antimony and two parts magnesium by weight was first prepared. The metals powdered to pass through a 40 M sieve were thoroughly mixed, placed in an iron tube, and heated in an atmosphere of hydrogen to a bright red heat, being finally kept at a dull red heat for about one hour. The alloy thus formed was easily removed from the tube, being in the form of a brown powder.

In preparing the stibine, the finely powdered alloy was gradually shaken into cold diluted hydrochloric acid. sp. gr., 1.06, which had previously been boiled to free it from air. The acid was kept cold during the reaction by shaking the generator which was immersed in a mixture of ice and brine. Before passing through the drying tubes of calcium chloride and phosphorus pentoxide the gas passed through moist glass wool and water in a U tube to absorb traces of hydrochloric acid that might be carried over mechanically from the gener-

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[1] Comptes rendus, 130, 1314, 1393 (1900).

[2] Complete details of preparation and photographs of the apparatus used as well as detailed data on the measurements are given by R. C. Palmer in his thesis for the degree of Chemical Engineer, University of Missouri, June 1910.

[3] Ber. chem. Ges., Berlin, 35, 2270 (1902).

[4] Ibid., 37, 885 (1904).

ator. With the exception of a piece of pressure tubing connecting the generator and drying train all connections were glass seals. Stock and Guttman experienced no difficulty in liquefying and solidifying stibine in a simple form of condenser immersed in liquid air. To liquefy stibine with Thilorier's mixture kept under diminished pressure we found it necessary to cool the gases in a spiral condenser ending in a small bulb at the bottom whose outlet passed up through the spirals and was surrounded by them. The liquid stibine was colorless and of high refractive power, and was easily transferred to the cells by distillation. The cells were finally sealed off at constricted places. We met with no accidents in these operations. Stock and Guttman state that gaseous and even liquid stibine have a tendency to dissociate with explosive violence. To prevent any explosion in sweeping back throughout the whole apparatus when the measuring cells were sealed off, a stopcock was placed between the condenser and the cell.

Only a faint antimony mirror appeared in the capillary tube where it was sealed off. The unstableness of stibine, however, was always manifest by the plating of antimony mirrors in different parts of the apparatus during an experiment.

Results.—The values obtained for the dielectric constants are summarized in the following table: Unless otherwise specified the values refer to the substances in the liquid state under their own vapor pressure at the temperature given.

Substance	Temp. ° C	D.C.	Temp. coeff. Percent
Ammonia	20.5	15.55	—
"	24.5	14.9	—
" (max. value)	—77	25.4	—0.4
" (solid)	—90	4.01	—
Phosphine	—60	2.55	+0.18
"	—25	2.71	—
" (calculated)	20	2.91	—
Stibine	—80	2.93	—
"	—50	2.58	—0.4
" (calculated)	20	1.76	—

The value obtained for liquid ammonia at 20.5°, 15.55, agrees fairly well with that of Coolidge, who found 16.2 at 14°, and also with the result of Goodwin and Thompson, namely 21–23 at —34°. From the dielectric constants at 20.5° and —77° the calculated temperature coefficient is —0.4% per degree rise in temperature referred to the maximum at —77°. The value of the dielectric constant for liquid ammonia at 20.5°, namely 15.55, if calculated to —34° by means of the temperature coefficient determined gives the value 21.4. This agrees fairly well with the value determined by Goodwin and Thompson for this temperature, namely 21–23. It should be stated in this connection that the cells used for making the measurements were designed for substances with low dielectric constants. Consequently the values determined for liquid ammonia are not as accurate as the apparatus is capable of giving.

The temperature coefficient of liquid phosphine was found to be positive, and has a value of 0.18% referred to the value at —60°. The dielectric constants for phosphine and stibine at 20° were calculated by assuming that the change in value is a linear function of the temperature.

The electrical conductivity of phosphine and stibine in the liquid state was tested and these solvents were found to be non-conductors like benzene.

It is hoped to complete this series of determinations by measuring the dielectric constant of liquid arsine.

Discussion.—It is seen from the results that the dielectric constants of the liquids determined, decrease with increase of molecular weight. Tereschin[1] showed that in a large number of cases of homologous series, such as organic acids, alcohols, etc., the dielectric constants decreased with increased molecular weight. This inorganic series, ammonia, phosphine, and stibine, may show this same relation although not an homologous series in the usual sense.

It was noted by Schlundt[2] that there is always a marked

[1] Wied. Ann., 36, 807 (1899).

[2] Bull. Univ. Wis. Sci. Series, 2, 353 (1901).

difference in the physical properties of the first two members of any homologous series, and that this difference always held for the value of the dielectric constant. This marked difference is also shown for the dielectric constants of liquid ammonia and liquid phosphine, the values being 15.55 and 2.91 respectively at 20° C. This fact assumes especial importance when it is considered that the nitrogen, phosphorus, and antimony compounds may be classed as organic as well as inorganic.

As regards the Nernst[1]-Thomson[2] rule very little can be said for the values determined, since the ionizing power of these liquids as solvents, with the exception of ammonia, have never been studied. Liquid ammonia is an excellent example of the Nernst-Thomson rule since its dielectric constant is comparatively high and its ionizing power as a solvent is quite marked. It would be expected that liquid phosphine and liquid stibine having low dielectric constants would show very little ionizing power. But in view of previous work[3] on liquid hydrogen halides which have low dielectric constants but do possess marked ionizing power, this property cannot be predicted for liquid phosphine and liquid stibine.

Chemical Laboratory,
University of Missouri,
December, 1910

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[1] Zeit. phys. Chem., 13, 531 (1894).
[2] Phil. Mag., [5] 36, 320 (1893).
[3] Jour. Phys. Chem., 13, 669 (1909).

STUDIES IN THE ELECTROCHEMISTRY OF THE PROTEINS, VI. THE CONDUCTIVITIES OF SOLUTIONS OF THE CASEINATES OF POTASSIUM AND OF THE ALKALINE EARTHS IN MIXTURES OF WATER AND ALCOHOL.

BY T. BRAILSFORD ROBERTSON

(From the Rudolf Spreckels Physiological Laboratory of the University of California)

I. Introduction

If one-half a cubic centimeter of a 0.0125 solution of KOH, neutralized either to phenolphthalein or to litmus by the addition of casein, be added to 10 cc, *i. e.*, to 20 volumes of 99.8 percent alcohol, no precipitation of protein occurs, although the solution which is thus obtained is appreciably more opalescent than a solution of equal concentration in water containing no alcohol. Even if, instead of employing a solution of potassium caseinate in water, we employ a 0.0125 solution of KOH in 75 percent alcohol, containing 1.6 or 2.5 percent of casein, adding $^1/_4$ cc of this to 10 cc of 99.8 percent alcohol, still no precipitation of the caseinate occurs, although it is now dissolved or forms a stable suspension in a 98.6 percent solution of alcohol. The caseinate can, however, be readily precipitated by adding to this mixture an equal volume of ether and allowing it to stand for a few hours.

Very different is the behavior of the caseinates of the alkaline earths. If to 100 cc each of 60, 70, 75 percent, etc., solutions of alcohol we add $^1/_2$ cc of a 0.012 N solution of $Ca(OH)_2$ neutralized to phenolphthalein by casein, distinct precipitation of the caseinate occurs, on shaking, when the final concentration of alcohol in the mixture is about 55 percent. The same is true for an equally concentrated solution of barium hydroxide neutralized to phenolphthalein by casein. For strontium caseinate, the limiting concentration of alcohol at which precipitation occurs is much higher,

about 70 percent. In all cases precipitation is much accelerated by energetic shaking of the mixture.

It is of interest to compare the marked difference between the behavior of the caseinates of the alkalies and of the alkaline earths upon the addition of alcohol to their aqueous solutions, with the numerous other differences which subsist between the caseinates of the alkalies and those of the alkaline earths.

Thus the aqueous solutions of the "neutral" or "basic" caseinates of the alkalies and ammonium are clear, do not (except lithium caseinate) show any increase in turbidity on warming, and are not precipitated by the addition of finely divided insoluble substances or by passing through a clay filter, while the aqueous solutions of the caseinates of the alkaline earths are opalescent, show a marked increase in turbidity on heating their solutions to 35°–45° C which disappears on cooling and are precipitated from their solutions by the addition of finely divided insoluble substances or by passage through a clay filter.[1]

The "neutral" and "basic" caseinates of the alkalies, upon solution in water, depress its freezing point and the amount of the depression is that of a solution of the molecular concentration as the alkaline solution which is employed as solvent. The depression produced by calcium caseinate is much less, being less than half as great.[2]

Equally concentrated solutions of the hydroxides of the alkalies and ammonium dissolve casein at approximately the same rate. Solutions of the hydroxides of the alkaline earths dissolve casein much more slowly.[3] The rate of the solution of casein by solutions of the hydroxides of the alkalies is accelerated by raising the temperature above 36°; the rate of the solution of casein by solutions of calcium hydroxide is materially diminished by a similar rise in temperature.[4]

[1] W. A. Osborne: Jour. Physiol., 27, 398 (1901).

[2] T. Brailsford Robertson and Theo. C. Burnett: Jour. Biol. Chem., 6, 105 (1909).

[3] T. Brailsford Robertson: Jour. Phys. Chem., 14, 377 (1910).

[4] T. Brailsford Robertson: Jour. Biol. Chem., 5, 147 (1908).

The caseinates of the alkaline earths are precipitated from their solutions by the addition of small concentrations of the chloride of the corresponding alkaline earth.[1]

The caseinates of the alkalies are not precipitated by the addition of similar quantities of the chlorides of the alkalies.

I have alluded to the fact that the limiting concentration of alcohol at which strontium caseinate is precipitated is considerably higher than that at which calcium and barium caseinates are precipitated. This is curious because we should expect, as a rule, to find the salts of strontium possessed of properties intermediate between those of calcium and barium. It is, therefore, the more interesting to observe that this is not the only respect in which the caseinates of strontium exhibit behavior differing from that of the caseinates of calcium and barium and approaching the behavior of the caseinates of the alkalies: for casein dissolves much more rapidly in solutions of strontium hydroxide than it does in equally concentrated solutions of calcium or barium hydroxide;[2] the solutions of strontium caseinate are less opalescent than equally concentrated solutions of calcium or barium caseinate, and the dissociation-constant of "basic" strontium caseinate is much larger than those of barium or calcium caseinate and is intermediate in magnitude between these and the dissociation-constants of the "basic" caseinates of sodium and ammonium. This, however, is not a *general* phenomenon where protein salts of the alkaline earths are concerned, because the dissociation constant for the strontium salt of "insoluble" serum globulin is not very appreciably different from those of the calcium and barium salts.[3]

It appeared of interest to determine the conductivities of solutions of the caseinates of potassium and of the alkaline earths in alcohol-water mixtures, not only with a view towards a further comparison of the caseinates of the alkalies and of the alkaline earths but also with a view towards a

[1] T. Brailsford Robertson: Jour. Phys. Chem., 13, 469 (1909).
[2] Ibid., 14, 377 (1910).
[3] Ibid., 15, 166 (1911).

further understanding of the chemical mechanics of the precipitation of proteins by alcohol.

II. Experimental

The mode of preparation of the casein and the technique of the conductivity determinations were the same as described in previous communications.[1] All of the conductivity determinations were made at 30° C. The resistance-capacity of the vessel employed was 0.1949. The conductivity of the distilled water, in reciprocal ohms per cc was 4×10^{-6} and it has been subtracted from each of the tabulated conductivities.

In five hundred cc of N/10 KOH were dissolved 62.5 grams of casein, thus forming a solution of "basic" potassium caseinate, neutral to phenolphthalein. To 50 cc portions of this solution were added, respectively, 0, 20, 40, etc., cc of alcohol and the mixtures were diluted to 200 cc with water. Each of these solutions was then diluted with alcohol solutions, of corresponding concentrations, to the desired concentration of caseinate. The solutions in " 75 percent alcohol" were made up by adding 99.8 percent alcohol to 50 cc of the original solution of caseinate until the volume was 200 cc, and diluting with a 75 percent by volume solution of 99.8 percent alcohol.

The following were the results obtained:

[1] T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

TABLE I

Alcohol 0 percent by volume		Alcohol 10 percent by volume		Alcohol 20 percent by volume		Alcohol 30 percent by volume	
Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°	Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°	Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°	Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°
0.0250	1648×10^{-6}	0.0250	1241×10^{-6}	0.0250	938×10^{-6}	0.0250	715×10^{-6}
0.0125	890×10^{-6}	0.0125	677×10^{-6}	0.0125	509×10^{-6}	0.0125	391×10^{-6}
0.0063	482×10^{-6}	0.0063	368×10^{-6}	0.0063	274×10^{-6}	0.0063	213×10^{-6}
0.0031	258×10^{-6}	0.0031	199×10^{-6}	0.0031	149×10^{-6}	0.0031	116×10^{-6}
0.0016	138×10^{-6}	0.0016	107×10^{-6}	0.0016	80×10^{-6}	0.0016	62×10^{-6}
Alcohol 40 percent by volume		**Alcohol 50 percent by volume**		**Alcohol 60 perc nt by volume**		**Alcohol 75 percent by volume**	
Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°	Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°	Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°	Equiv. conc. of KOH neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°
0.0250	554×10^{-6}	0.0250	429×10^{-6}	0.0250	319×10^{-6}	0.0250	130×10^{-6}
0.0125	305×10^{-6}	0.0125	240×10^{-6}	0.0125	182×10^{-6}	0.0125	94×10^{-6}
0.0063	171×10^{-6}	0.0063	131×10^{-6}	0.0063	101×10^{-6}	0.0063	59×10^{-6}
0.0031	92×10^{-6}	0.0031	74×10^{-6}	0.0031	58×10^{-6}	0.0031	37×10^{-6}
0.0016	49×10^{-6}	0.0016	39×10^{-6}	0.0016	30×10^{-6}	0.0016	20×10^{-6}

Twenty grams of casein were dissolved in 200 cc of 0.05 N KOH. To twenty-five cc portions of this solution were added 10, 20, etc., of alcohol and the mixtures thus obtained were diluted to 100 cc. The solution in 75 percent alcohol being obtained by adding 99.8 percent alcohol to 25 cc of the original solution of caseinate until the total volume of the mixture attained 100 cc.

TABLE II

Concentration of KOH neutralized to litmus by casein = 0.0 125

Percent alcohol by volume	x = conductivity in reciprocal ohms per cc at 30°
0	866×10^{-6}
10	663×10^{-6}
20	513×10^{-6}
50	254×10^{-6}
75	80×10^{-6}

Fifteen grams of casein were dissolved in 250 cc of 0.048 N $Ca(OH)_2$, thus forming a solution of "basic" calcium caseinate. To 25 cc portions of this solution were added 0, 10, 20, etc., cc of alcohol and these mixtures were diluted to 100 cc. It was found preferable to pour the caseinate solution into the alcohol (previously somewhat diluted) rather than to pour the alcohol into the caseinate solution for otherwise coagula were formed where the concentrated alcohol first met the caseinate solution and these coagula redissolved with difficulty.

The following were the results obtained:

TABLE III

Concentration of $Ca(OH)_2$ neutralized to phenolphthalein by casein = 0.012 N

Percent of alcohol by volume	x = conductivity in reciprocal ohms per cc at 30°
0	177×10^{-6}
10	75×10^{-6}
20	37×10^{-6}
30	22×10^{-6}
40	16×10^{-6}
50	12×10^{-6}

Fifteen grams of casein were dissolved in 500 cc of 0.024 N $Sr(OH)_2$, thus forming a solution of "basic" strontium caseinate. To 50 cc samples of this solution were added 0, 10, 20, etc., cc of alcohol and the mixture were diluted to 100 cc.

The following were the results obtained:

TABLE IV

Concentration of $Sr(OH)_2$ neutralized to phenolphthalein by casein = 0.012 N

Percent of alcohol by volume	x = conductivity in reciprocal ohms per cc at 30°
0	251×10^{-6}
10	124×10^{-6}
20	63×10^{-6}
30	42×10^{-6}
40	32×10^{-6}
50	23×10^{-6}

Fifteen grams of casein were dissolved in 250 cc of 0.028 N $Ba(OH)_2$, thus forming a solution of "basic" barium caseinate. To 25 cc portions of this were added 0, 10, 20, etc. cc of alcohol and these mixtures were diluted to 100 cc.

The following were the results obtained:

TABLE V

Concentration of $Ba(OH)_2$ neutralized to phenolphthalein by casein = 0.012 N.

Percent of alcohol by volume	x = conductivity in reciprocal ohms per cc at 30°
0	167×10^{-6}
10	66×10^{-6}
20	30×10^{-6}
30	17×10^{-6}
50	7×10^{-6}

The solutions of calcium and barium caseinates in 50 percent alcohol were very opalescent, that of the Ba casein-

ate being as opaque as milk. The solution of strontium caseinate in 50 percent alcohol was much less opalescent. In the solutions of "basic" potassium caseinate it was observed that the opalescence underwent a marked and relatively sudden increase at a concentration of alcohol lying between 60 percent and 75 percent by volume, although, as we have seen, precipitation of the caseinate did not occur at even very much higher concentrations of alcohol.

III. Discussion of the Results and Additional Data

(*i*) *The applicability of the Ostwald dilution-law to solutions of the caseinates in alcohol-water mixtures.*

In previous communications I have shown[1] that the Ostwald dilution-law for a binary electrolyte may be written:

$$m = \frac{1.037 \times 10^{-2}}{v_1 + v_2} x + \frac{1.075 \times 10^{-4}}{G(v_1 + v_2)^2} x^2 \quad \ldots\ldots\ldots (1)$$

where m is the equivalent-molecular concentration of the electrolyte, x is its conductivity in reciprocal ohms per cc, G its dissociation constant and v_1 and v_2 are the ionic velocities in cm per sec. per potential gradient of 1 volt per cm. In the same communications I have shown that this law, in the form

$$m = \frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)} x + \frac{1.075 \times 10^{-4}}{G\rho(v_1 + v_2)^2} x^2 \quad \ldots\ldots\ldots (2)$$

where m is the equivalent-concentration of base combined with the protein and ρ is the number of equivalent gram molecules of caseinate which is produced by the neutralization of one equivalent gram molecule of base, holds good for aqueous solutions of the "neutral" and "basic" caseinates of sodium and ammonium and for solutions of the "basic" caseinates of calcium, barium and strontium. From these and other data I have concluded[2] that in the formation of the "basic" caseinates two (or four) molecules of base are

[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907); 12, 473 (1908); 14, 601 (1910).

[2] Ibid., 14, 528, 601 (1910).

bound up in one molecule of caseinate and that the salt which is thus formed dissociates into two (or four) quadrivalent ions.

Applying equation (2) to the results enumerated in Table I and computing the constants $\frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)}$ and $\frac{1.075 \times 10^{-4}}{G\rho(v_1 + v_2)^2}$ for each concentration of alcohol from all the results by the method of least squares, we obtain:

For the solutions containing 0 percent of alcohol:

$$m = 12.41\ x + 1666\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

For the solutions containing 10 percent of alcohol:

$$m = 15.97\ x + 3325\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

For the solutions containing 20 percent of alcohol:

$$m = 21.14\ x + 5880\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

For the solutions containing 30 percent of alcohol:

$$m = 27.23\ x + 10858\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

For the solutions containing 40 percent of alcohol:

$$m = 34.63\ x + 18931\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

For the solutions containing 50 percent of alcohol:

$$m = 42.91\ x + 35937\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

For the solutions containing 60 percent of alcohol:

$$m = 53.49\ x + 78335\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

For the solutions containing 75 percent of alcohol:

$$m = 29.95\ x + 1219800\ x^2 \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Inserting in these equations the observed values of x, we can compute the "theoretical" values of m, that is, the equivalent concentrations of KOH neutralized by the casein which should, provided that in all of these solutions, potassium caseinate dissociates into two ions (or into *four* ions all capable of mutual interaction, Cf. part V of these "Studies" Journal of Physical Chem.) correspond to the observed conductivities. In the following table the observed and calculated values of m are compared:

TABLE VI

Alcohol = 0 percent			Alcohol = 10 percent			Alcohol = 20 percent			Alcohol = 30 percent		
$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ	$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ	$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ	$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ
250	240	0	250	250	0	250	251	+ 1	250	250	0
125	124	— 1	125	123	— 2	125	123	— 2	125	123	— 2
63	64	+ 1	63	63	0	63	62	— 1	63	63	0
31	33	+ 2	31	33	+ 2	31	33	+ 2	31	32	+ 1
16	16	0	16	17	+ 1	16	17	+ 1	16	17	+ 1
	Σ Δ	+ 2		Σ Δ	+ 1		Σ Δ	+ 1		Σ Δ	0

Alcohol = 40 percent			Alcohol = 50 percent			Alcohol = 60 percent			Alcohol = 75 percent		
$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ	$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ	$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ	$m \times 10^4$ observed	$m \times 10^4$ calculated	Δ
250	250	0	250	250	0	250	251	+ 1	250	245	— 5
125	123	— 2	125	124	— 1	125	124	— 1	125	136	+ 11
63	63	0	63	62	— 1	63	62	— 1	63	62	— 1
31	34	+ 3	31	34	+ 3	31	34	+ 3	31	28	— 3
16	17	+ 1	16	17	+ 1	16	17	+ 1	16	11	— 5
	Σ Δ	+ 2		Σ Δ	+ 2		Σ Δ	+ 3		Σ Δ	— 3

It is evident that the correspondence between the experimenta results and those which are indicated by the Ostwald dilution-law for a binary electrolyte is all that could be desired for the solutions containing from 0 to 60 percent of alcohol. For the solutions containing 75 percent of alcohol, the divergences between theory and experiment are, however, considerably greater than could be accounted for by experimental error and probably indicate that the law does not hold good for these solutions. The sudden alteration in the relative values of the constants which occurs when the percentage of alcohol attains this magnitude indicates, whether the Ostwald law be considered as holding good or not, a profound change in the molecular and ionic condition of the protein.

It would appear, however, that we are justified in concluding that potassium caseinate dissociates in alcohol-water mixtures containing from 0 to 60 percent of alcohol in the same manner as it does in aqueous solutions.

(*ii*) *The influence of the concentration of alcohol in the solvent upon the conductivities of solutions of potassium caseinate.*

I find that the conductivity ($\equiv x_y$) of a solution containing any given concentration of casein combined with KOH in the proportion requisite, in aqueous solution, to secure neutrality to phenolphthalein, when dissolved in an alcohol-water mixture containing y percent of alcohol by volume is connected with the conductivity ($\equiv x_0$) of a similar solution in water by the formula

$$x_y = \frac{x_0}{A^y} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

where A is a constant which varies but slightly, if at all, with the concentration of the caseinate. This constant is determined in the following manner: If the logarithms to base 10 of x corresponding to y = 0, 10, 20, 30, 40, 50 and 60 percent be tabulated in order and each successive value of log x be subtracted from the one lying immediately above

it, the differences thus computed are observed to be appreciably constant and equal to ten times the log, to base 10 of A. For all of the determinations enumerated in Table I (omitting, in the computation, the solutions containing 75 percent alcohol) the average value of A is 1.0265. For the various concentrations of potassium caseinate the values of A are as follows:

TABLE VII

Concentration of KOH neutralized by casein	A
0.0250	1.1279
0.0125	1.0270
0.0063	1.0265
0.0031	1.0252
0.0016	1.0257
	Average, 1.0265

In the accompanying table (Table VIII) the experimental values of x and those computed from the formula $x_y = \frac{x_0}{A^y}$ are compared. Two "calculated" values of x_y are given, the first calculated value of x_y being computed from the average value of A for the concentration of caseinate in the solutions under consideration, the second being computed from the average value of A for all the determinations enumerated in Table I, with the omission, of course, of those for the solvent containing 75 percent of alcohol.

The same relation also holds good for solutions of "neutral" potassium caseinate in alcohol-water mixtures, in this case the values of A were computed from the results (except that for 75 percent alcohol) enumerated in Table II, the average difference in $\log_{10} x_y$ for 10 percent increase in y being computed by adding together the three observed differences (between x_y, corresponding to $y = 0$ percent and 10 percent, 10 percent and 20 percent, 20 percent and 50 percent) and dividing their sum by 5. In this way A is ascertained to possess, for these solutions, the average value

TABLE VIII

Concentration of KOH neutralized by casein 0.0250				Concentration of KOH neutralized by casein 0.0125				Concentration of KOH neutralized by casein 0.0063				Concentration of KOH neutralized by casein 0.0031				Concentration of KOH neutralized by casein 0.0016			
y	$x_y \times 10^5$ obs.	$x_y \times 10^5$ calc. $A = 1.0279$	$x_y \times 10^5$ calc. $A = 1.0265$	y	$x_y \times 10^5$ obs.	$x_y \times 10^5$ calc. $A = 1.0270$	$x_y \times 10^5$ calc. $A = 1.0265$	y	$x_y \times 10^5$ obs.	$x_y \times 10^5$ calc. $A = 1.0265$	$x_y \times 10^5$ calc. $A = 1.0265$	y	$x_y \times 10^5$ obs.	$x_y \times 10^5$ calc. $A = 1.0252$	$x_y \times 10^5$ calc. $A = 1.0265$	y	$x_y \times 10^5$ obs.	$x_y \times 10^5$ calc. $A = 1.0257$	$x_y \times 10^5$ calc. $A = 1.0265$
0	165	165	165	0	89	89	89	0	48	48	48	0	25.8	25.8	25.8	0	13.8	13.8	13.8
10	124	125	127	10	68	68	68	10	37	37	37	10	19.9	20.1	19.8	10	10.7	10.7	10.6
20	94	95	98	20	51	52	53	20	27	28	28	20	14.9	15.7	15.3	20	8.0	8.3	8.2
30	72	72	75	30	39	40	41	30	21	22	22	30	11.6	12.2	11.8	30	6.2	6.4	6.3
40	55	55	58	40	31	31	31	40	17	17	17	40	9.2	9.5	9.0	40	4.9	5.0	4.8
50	43	42	45	50	24	23	24	50	13	13	13	50	7.4	7.4	7.0	50	3.9	3.9	3.7
60	32	32	34	60	18	18	19	60	10	10	10	60	5.8	5.8	5.4	60	3.0	3.0	2.9
75	13	21	23	75	9	12	13	75	6	7	7	75	3.7	4.0	3.6	75	2.0	2.1	1.9

1.0248. In the following table the actual and computed values of x_y are compared:

TABLE IX

Concentration of KOH neutralized by casein = 0.0125

y	$x_y \times 10^{-5}$ observed	$x_y \times 10^{-5}$ calculated
0	87	87
10	66	68
20	51	53
50	25	25
75	8	14

The law does *not*, however, hold good for solutions of the caseinates of the alkaline earths in alcohol-water mixtures; this is evidenced by the lack of constancy in the first differences of $\log_{10} x_y$ corresponding to equal increments of y. In the accompanying table are given the values of $\log_{10} x_y$ corresponding to various values of y for the solutions of calcium caseinate, computed from the results enumerated in Table III.

TABLE X

y = percent of alcohol by volume	$\text{Log}_{10} x_y \times 10^5$	Difference
0	1.24797	—
10	0.87506	0.37291
20	0.56820	0.30686
30	0.34242	0.22578
40	0.20412	0.13830
50	0.07918	0.12494

In the following table are given the corresponding data for strontium caseinate derived from Table IV:

TABLE XI

y = percent of alcohol by volume	$\text{Log}_{10} x_y \times 10^5$	Difference
0	1.39967	—
10	1.09342	0.30625
20	0.79934	0.29408
30	0.62325	0.17609
40	0.50515	0.11810
50	0.36173	0.14342

It is perhaps not without significance that in the above table the first two differences are much more nearly alike than the succeeding differences. In solutions containing 0 to 25 percent of alcohol strontium caseinate is further from precipitation than corresponding solutions of calcium caseinate and, as we have A, in the equation $x_y = \frac{x_o}{A^y}$, approaches constancy. Having regard to the observed failure of the solutions of potassium caseinate in 75 percent alcohol to conform to the law, and to the fact that at an alcohol-concentration lying between 60 percent and 75 percent solutions of potassium caseinate undergo a great and relatively sudden increase in opacity, we may, I think, conclude that *the precipitation of a caseinate by alcohol is heralded by a failure of the solution to conform to the law* $x_y = \frac{x_o}{A^y}$, *connecting the percentage of alcohol in solution with its conductivity.*

(*iii*) *The interpretation of the law* $x_y = \frac{x_o}{A^y}$.

As we have observed, the value of A is not only constant for all dilutions of potassium caseinate, but also is very nearly constant for all of the proportions of alcohol to water employed as solvents. Provided A was rigorously constant we would obviously obtain the relation:

$$\frac{x_{H_2O}}{x_{alc.\ H_2O}} = \text{constant}$$

for any given proportion of alcohol to water. This is the relation, suggested by Cohen,[1] connecting the conductivities of inorganic salts in mixtures of alcohol and water. Roth,[2] however, found that this rule does not strictly hold good for solutions of KCl in mixtures of alcohol and water, but that the quotient $\frac{x_{H_2O}}{x_{alc.\ H_2O}}$ decreases somewhat with increasing dilution. In the accompanying table, the values of $\frac{x_{H_2O}}{x_{alc.\ H_2O}}$ are given for each of the proportions of alcohol to H_2O employed.

[1] Cohen: Zeit. phys. Chem., 25, 31 (1898).
[2] Roth: Ibid., 42, 209 (1903).

TABLE XII

Alcohol 10 percent		Alcohol 20 percent		Alcohol 30 percent		Alcohol 40 percent	
Equivalent concentration of KOH neutralized by casein	$\frac{x_{H_2O}}{x_{alc.\ H_2O}}$	Equivalent concentration of KOH neutralized by casein	$\frac{x_{H_2O}}{x_{alc\ H_2O}}$	Equivalent concentration of KOH neutralized by casein	$\frac{x_{H_2O}}{x_{alc.\ H_2O}}$	Equivalent concentration of KOH neutralized by casein	$\frac{x_{H_2O}}{x_{alc.\ H_2O}}$
0.0250	1.33	0.0250	1.76	0.0250	2.31	0.0250	2.98
0.0125	1.31	0.0125	1.75	0.0125	2.28	0.0125	2.92
0.0063	1.31	0.0063	1.76	0.0063	2.26	0.0063	2.82
0.0031	1.30	0.0031	1.73	0.0031	2.22	0.0031	2.80
0.0016	1.29	0.0016	1.73	0.0016	2.22	0.0016	2.82

Alcohol 50 percent		Alcohol 60 percent		Alcohol 75 percent	
Equivalent concentration of KOH neutralized by casein	$\frac{x_{H_2O}}{x_{alc.\ H_2O}}$	Equivalent concentration of KOH neutralized by casein	$\frac{x_{H_2O}}{x_{alc.\ H_2O}}$	Equivalent concentration of KOH neutralized by casein	$\frac{x_{H_2O}}{x_{alc.\ H_2O}}$
0.0250	3.84	0.0250	5.17	0.0250	12.70
0.0125	3.71	0.0125	4.89	0.0125	9.47
0.0063	3.68	0.0063	4.77	0.0063	8.19
0.0031	3.49	0.0031	4.45	0.0031	6.98
0.0016	3.54	0.0016	4.60	0.0016	6.90

It will be observed that the values of $\frac{x_{H_2O}}{x_{alc.\ H_2O}}$ are appreciably constant for each proportion of alcohol to water, for the solutions containing 0 to 60 percent of alcohol, but that in the solutions containing 75 percent of alcohol the value of this ratio does not even approximate to constancy but decreases rapidly. There is, it is true, a slight but regular diminution in the value of this ratio, even in the solution containing 0 to 60 percent of alcohol, in passing from an equivalent concentration of neutralized KOH of 0.0250 to 0.0016, but, except in the solutions containing 75 percent alcohol, the diminution is not more than a few percent.

We have seen (equns. 3 to 10) that the Ostwald dilution-law, in the form expressed in equation (2) holds good, at any rate for solutions of potassium caseinate in alcohol-water mixtures containing 0 to 60 percent of alcohol.

From the symmetry of the equation:

$$m = \frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)} x + \frac{1.075 \times 10^{-4}}{G\rho(v_1 + v_2)^2} x^2$$

it would follow, were A strictly constant for all dilutions, that the proportion of alcohol to water employed as solvent for the caseinate affects only $v_1 + v_2$, *i. e.*, the migration-velocities of the ions, not the dissociation-constant ($\equiv$G) or the number of equivalents of caseinate resulting from the neutralization of one molecule of KOH ($\equiv\rho$). Since the alteration in A with dilution of the potassium caseinate is so small for solvents containing 0 to 60 percent of alcohol, we may conclude that in these solutions it is for the greater part the migration-velocity of the caseinate ions which is affected by the percentage of alcohol in the solvent. From the values of the constants in equations 3–9, it is apparent that the migration velocities of the caseinate ions are progressively *diminished* by increasing alcohol-concentration from 0 percent to 60 percent. From the facts that the law $x_y = \frac{x_0}{A^y}$ no longer holds good and the ratio $\frac{x_{H_2O}}{x_{alc.\ H_2O}}$ is not constant in the solutions containing 75 percent alcohol, we may con-

clude that in these solutions the degree of dissociation of the caseinate or the number of equivalents of casein produced by one equivalent of KOH or both undergo a profound modification. The values of the constants in equation 10 indicating an *increase* in the magnitude of $v_1 + v_2$ and a very great *decrease* in the magnitude of the dissociation-constant. In the following table the values of $(v_1 + v_2)$ and of $\frac{G}{\rho}$ corresponding to the equations 3-10 are enumerated: in the fourth column is given the percentage dissociation of the caseinate in the solution containing 0.025 N KOH bound by casein.

TABLE XIII

Potassium caseinate 80 × 10^{-5} equivalents of KOH per gram

Percent of alcohol by volume	$\rho(v_1 + v_2)$	$\frac{G}{\rho}$	Percent of caseinate dissociated in solution containing 0.025 equivalents of potassium
0	83.6 10^{-5}	0.0923	82
10	64.9 10^{-5}	0.0767	80
20	49.1 10^{-5}	0.0760	79
30	38.0 10^{-5}	0.0682	78
40	29.9 10^{-5}	0.0633	77
50	24.2 10^{-5}	0.0513	74
60	19.4 10^{-5}	0.0365	68
75	34.6 10^{-5}	0.0007	17

The degrees of dissociation of the caseinates in the solutions containing 60 percent and less than 60 percent of alcohol is evidently but little effected by the percentage of alcohol in the solvent, the major part to the effect of the alcohol upon the conductivity being attributable to the decreased mobility of the caseinate ions.

(iv) *The viscosities of solutions of "basic" potassium caseinate in alcohol-water mixtures.* The striking resemblance between the formula $\frac{x_y}{x_o} = \frac{1}{A^y}$ and the Arrhenius-Euler formula: $\frac{\eta_n}{\eta_o} = \alpha^n$ for the dependence of the viscosity of a solution upon its concentration where η_n is the viscosit

of the solution, η_o that of the solvent, n is the concentration of the solution and a is a constant, forcibly suggests that the decrease in the conductivity of potassium caseinate solutions, due to the addition of alcohol between alcohol-percentages of 0 and 60 may be attributed for the greater part to the hampering of the protein ions by the increased internal friction of the solvent.[1]

Accordingly the following determinations were made: 31.25 grams of casein were dissolved in 250 cc of $N/10$ KOH. To 25 cc portions of this were added 0, 10, 20, etc. cc of alcohol, the volume of each mixture being made up to 100 cc, the solution containing 75 percent alcohol being made up by adding 99.8 percent alcohol until the volume of the mixture was 100 cc.

A series of exactly similar solutions were made up in which, however, 25 cc of N/10 KOH were employed instead of 25 cc of caseinate solution.

The viscosities of these solutions were determined at 30° in an Ostwald viscometer, for which the time of outflow, for water, was 90 seconds. The times of flow, were read with a stop-watch. The viscosities were calculated from the formula $\frac{\eta}{\eta_o} = \frac{st}{s_o t_o}$ where η_o is the viscosity of distilled water, η that of the solution under investigation, $= s_o$ and t_o are the density and time of outflow, respectively, of distilled water and s and t are the density and time of outflow, respectively of the solution. The densities of the solutions were determined by means of a normal hydrometer, reading the density to within 0.0002.

Taking the viscosity of water at 30° to be 0.00798 dynes per cc[2] and its density as 0.996, the following were the results obtained:

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[1] In this connection the work of H. C. Jones and collaborators on the conductivities of solutions of inorganic salts in alcohol-water and acetone-water mixtures should be consulted. Am. Chem. Jour., 28, 329 (1902); 32, 521 (1904); 34, 481 (1905); 36, 325, 427 (1906); 37, 405 (1907); Zeit. phys. Chem., 61, 641; 62, 41 (1908); Am. Chem. Jour., 41, 433 (1909); 42, 37 (1909); cf. also Walden: Zeit. phys. Chem., 55, 207 (1906); Heber Green: Jour. Chem. Soc.

[2] Thorpe and Rodger: Phil. Trans., 185A, 307 (1894).

TABLE XIV

Concentration of KOH neutralized to phenolphthalein by casein = 0.250 N

Percent of alcohol by volume	η in dynes per cc for solvent	η in dynes per cc for solution	Difference due to caseinate
0	0.00816	0.01668	0.00852
10	0.01065	0.02049	0.00984
20	0.01376	0.02484	0.01108
30	0.01694	0.02814	0.01120
40	0.01913	0.03237	0.01324
50	0.02064	0.03400	0.01336
60	0.02011	0.03200	0.01189
75	0.01735	0.02345	0.00610

Walden (l. c.) has found that for solutions of tetraethylammonium iodide in thirty organic solvents the product of the molecular conductivity of the salt at infinite dilution is proportional to $v_1 + v_2$ (the sum of the migration-velocity of its ions) and the viscosity of its infinitely dilute solution is nearly constant, indicating an inverse proportionality between the viscosity of the solution (or, which comes to the same thing at infinite dilution, the solvent) and the migration-velocities of the ions which it contains. In the accompanying table are given the values of $\rho(v_1 + v_2)\eta_{solvent}$ for the various solutions investigated.

TABLE XV

Percent of alcohol by volume	$\rho(v_1 + v_2)\eta_{solvent}$
0	0.68×10^{-5}
10	0.69×10^{-5}
20	0.68×10^{-5}
30	0.64×10^{-5}
40	0.57×10^{-5}
50	0.50×10^{-5}
60	0.39×10^{-5}
75	0.60×10^{-5}

It is evident that the product of the ionic mobility of potassium caseinate at infinite dilution and the viscosity of

the solvent varies much less than either of these quantities taken alone, indicating in a qualitative sense at all events, that *the ionic mobility of the caseinate is in the main determined by the viscosity of the solvent.* The observed *increase* in the ionic mobility of the caseinate ions on increasing the alcohol-content of the solvent from 60 percent to 75 percent, is, in view of the fact that the viscosity of the solvent passes through a maximum at 50 percent to 60 percent alcohol and rapidly decreases between 60 percent and 75 percent, especially confirmatory of this view. It will be observed that the viscosity of the solvent is notably increased by the addition of the concentration of casein employed and this effect, of course, varied very considerably with dilution, yet the Ostwald law holds good. We can only conclude from this that the viscosity of the solution, due to the casein *per se*, does not affect the mobility of the caseinate ions.[1]

(*v*) *The molecular condition of potassium caseinate in 75 percent alcohol.*

We have seen that the behavior, optical and electrical, of potassium caseinate dissolved in alcohol-water mixtures undergoes an abrupt change[2] in passing from 60 percent to 75 percent alcohol-content. The degree of dissociation, which is but little effected by lower concentrations of alcohol undergoes a profound diminution in 75 percent and the opacity of the solution undergoes a concurrent increase. These phenomena suggest a polymerization of the caseinate molecule and an accompanying increase in the weight of casein involved in the carriage of one atomic charge. Accordingly, experiments were undertaken with a view to ascertaining the effect of increasing alcohol-content of the solvent upon the electrochemical equivalent of casein.

The experiments were carried out upon solutions con-

[1] Cf. also Sackur: Zeit. phys. Chem., 41, 672 (1902); T. Brailsford Robertson: Jour. Phys. Chem., 12, 473 (1908).

[2] Not only is the opalescence of the solution greatly increased but also the change in the refractive index of the solvent due to the introduction of 1 gram of casein, is considerably diminished. T. Brailsford Robertson: Jour. Biol. Chem.

taining 50 percent and 75 percent of alcohol, made up in the manner described above. The electrochemical equivalent of casein, combined with potassium, in *aqueous* solution has previously been determined, and the methods employed in this were identical with those employed in the previous investigation.[1]

The alteration in the percentage casein-content of the solution, due to deposition of the casein upon the anode was estimated from the change in the refractive index of the solution. The volume of the solution employed being always 25 cc, the actual amount of casein deposited was obtained by dividing the alteration in percentage by 4. The change in the refractive indices of alkaline 50 percent and 75 percent alcohol solutions, due to the addition of casein had been previously determined by me[2] and I have, furthermore, shown that the change is directly proportional to the percentage of casein dissolved in these solvents.

The quantity of electricity which had traversed the solution was estimated by a silver titration voltameter, containing N/10 $AgNO_3$, placed in series with the solution under investigation.

The results obtained are tabulated below, the figures in the 6th column being obtained from those in the 5th column through multiplication by the Faraday constant.

There is evidently a very marked increase in the weight, or decrease in the valency of casein ions in solutions of basic potassium caseinate when the added alcohol attains 75 percent, leading to doubling of the weight of casein required to transport one atomic charge of electricity.

From these facts and from the failure of Ostwald's dilution law to adequately represent the behavior towards dilution of solutions of "basic" potassium caseinate in 75 percent

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 15, 179 (1911).

[2] T. Brailsford Robertson: Jour. Biol. Chem. For immediate reference the figures are repeated here: In 50 percent alcohol, change due to 1 gram per 100 cc = 0.00149 ± 0.00005. In 75 percent alcohol, change due to 1 gram 100 cc = 0.00125 ± 0.00006.

TABLE XVI[1]

50×10^{-5} Equivalents of KOH per gram of casein. Concentration of KOH neutralized by casein = 0.015 N

Percent of alcohol	Current in amperes	Time of passage	Grams casein lost from solution	Electrochemical equivalent in grams per coulomb	Grams of casein carrying one ionic charge
0	—	—	—	—	2336 ± 183
50	$6.88 \quad 10^{-4}$	3 hrs. 25 min.	0.2550 ± 0.0170	0.0301 ± 0.0020	2906 ± 193
75	$1.94 \quad 10^{-4}$	4 hrs. 0 min.	0.1260 ± 0.0200	0.0452 ± 0.0072	4363 ± 695

[1] The weight of casein, in grams, which carries one atomic charge, in aqueous solutions, is cited after my previous paper (loc. cit.).

The amount of casein lost from the anode through re-solution in electrolysis is not allowed for in the above estimates. In solutions containing alcohol, it is probably very small, since the rate of solution of casein in alkaline solvents is much diminished by alcohol.

The smallness of the current employed in the electrolysis of the solution containing 75 percent alcohol was due to the high resistance of the caseinate solution.

The precipitate from the solution containing alcohol is slimy and not spongy as it is from aqueous solution. Nor, in 75 percent alcohol, does it adhere well to the anode so that precipitation appears to take place in the body of the anodal portion of the fluid, and the solution had to be filtered to remove the casein precipitated by the electrolysis.

alcohol and the optical appearance of these solutions it appears probable that they partake rather of the character of suspensions than of true solutions and that the transport of electricity by the caseinate in 75 percent alcohol is a phenomenon of "electric endosmose."

The precipitation of a protein by alcohol is evidently heralded by, and is probably attributable to polymerization and greatly decreased dissociation of the protein salts.

Conclusions

(1) Potassium caseinate is not precipitated by the addition of alcohol to its solution up to 98.6 percent, but the solutions undergo a marked increase in opacity at a concentration of alcohol lying between 60 percent and 75 percent.

(2) The caseinates of the alkaline earths are precipitated by the addition of alcohol to their (aqueous) solutions. Calcium and barium caseinate are precipitated when the concentration of alcohol attains about 50 percent. For the precipitation of strontium caseinate, a somewhat higher concentration of alcohol is required, about 70 percent.

(3) The conductivities of solutions of varying casein-content in various alcohol-water mixtures have been determined.

(4) Solutions of potassium caseinate (proportion of KOH to casein $= 80 \times 10^{-6}$ equivalents per gram) in alcohol-water mixtures containing from 0 to 60 percent of alcohol obey Ostwald's dilution-law for a binary electrolyte. Solutions in 75 percent alcohol do not obey the law.

(5) The conductivity ($\equiv x_y$) of a solution containing any given concentration of the protein potassium caseinate is connected with the percentage ($\equiv y$) of alcohol in the solution (from 0 to 60 percent) and the conductivity ($\equiv x_0$) of a solution containing no alcohol by the formula $x_y = \frac{x_0}{A^y}$.

(6) The value of A is very nearly the same for all concentrations of potassium caseinate, and for all proportions of alcohol to water, between 0 and 60 percent, the average

being 1.0265, and departures from the average less than two-tenths of a percent.

(7) This law also holds good for solutions of "neutral" potassium caseinate (50×10^{-5} equivalents of KOH per gram) in alcohol-water mixtures containing less than 75 percent alcohol.

(8) The law also holds good for solutions of strontium caseinate from 0 to 20 percent of alcohol, but it does not hold good for solutions containing higher percentages of alcohol, nor for solutions of calcium or barium caseinates in alcohol-water mixtures nor for solutions of potassium caseinate in 75 percent alcohol.

(9) It is concluded that the precipitation of a caseinate by alcohol is heralded by a failure of the solution to conform to the law $x_y = \frac{x_0}{A^y}$.

(10) In solutions of "basic" potassium caseinate (80×10^{-5} equivalents of KOH per gram) containing from 0 to 60 percent of alcohol, the relation

$$\frac{x_{H_2O}}{x_{alc.\ H_2O}} = \text{constant}$$

holds good for any given proportion of alcohol to water. This relation implies that the effect of added alcohol (up to 60 percent) upon the conductivity of a caseinate solution is almost entirely attributable to its effect upon the mobility of the caseinate ions and not to any effect upon the dissociation or polymerization of the caseinate. It is the relation found by Cohen to hold good for the conductivities of solutions of inorganic salts in alcohol-water mixtures.

(11) In solutions containing 75 percent alcohol, the relation

$$\frac{x_{H_2O}}{x_{alc.\ H_2O}} = \text{constant}$$

does not hold good. It is inferred that in this concentration the alcohol exerts a considerable influence upon the dissociation or polymerization or both, of potassium caseinate.

(12) The relative ionic mobilities at infinite dilution and degrees of dissociation of "basic" potassium caseinate in alcohol-water mixture have been computed.

(13) The viscosities of solutions or "basic" potassium caseinate in alcohol-water mixtures and of these solvents have been determined.

(14) The relative ionic mobilities of "basic" potassium caseinate at infinite dilution in alcohol-water mixtures tend to be (but are not exactly) inversely proportional to the viscosities of the solvents.

(15) The mobility of the caseinate ions is not affected by that proportion of the viscosity of the solution which is due to the caseinate itself.

(16) It is inferred that up to and including 60 percent alcohol the major part of the effect of added alcohol upon the conductivity of "basic" potassium caseinate solutions is attributable to the greater or less degree to which the viscosity of the solvent diminishes the mobility of the caseinate ions.

(17) The electrochemical equivalents of casein combined with 80×10^{-5} equivalents of KOH per gram and dissolved in 50 percent and 75 percent alcohol have been determined. The weight of casein required to transport one ionic charge has been deduced, with the following results: In 0 percent alcohol the weight of casein required to transport one atomic charge is 2336 ± 183 grams; in 50 percent alcohol the weight of casein required to transport one atomic charge is 2906 ± 193 grams; in 75 percent alcohol the weight of casein required to transport one atomic charge is 4363 ± 695 grams.

(18) It is inferred that in 75 percent alcohol the major part of the effect of the added alcohol upon the conductivities of "basic" potassium caseinate solutions is attributable to polmerization of the caseinate and to a profound decrease in its degree of dissociation.

(19) It is concluded that the "solution" of potassium caseinate in 75 percent alcohol is probably to be regarded rather as a suspension than as a true solution and that the

transport of electricity by the caseinate in 75 percent alcohol is probably a phenomenon of "electric endosmose" rather than of true electrolytic conduction.

(20) The precipitation of protein salts by alcohol is attributed partly to polymerization and partly to greatly decreased dissociation of the salts.

(21) This explains the observed fact that alcohol precipitates protein salts as such from their solutions and not the uncombined proteins, since, previously to their precipitation, the combined base or acid is bound up in an undissociated molecule.

NEW BOOKS

Das Oedem. *By Martin H. Fischer. 24 × 16 cm; pp. vii + 223. Dresden: Verlag von Theodor Steinkopff, 1910. Price: paper, 6 marks. Cloth, 7 marks.*—This is a scientific study of the conditions under which water is taken up by living tissue. As it is essentially a problem in colloid chemistry the author studies the action of water and of solutions on fibrine and on gelatine. He then points out the parallelism between these cases and that of the adsorption of water by protoplasm. Special cases of oedema come next, followed by chapters on turgor and on the secretion of urine.

Of special interest to the physical chemist are the pages, 84–96, in which the author takes exception to the osmotic pressure theory as applied to plant cells. He claims that there is no evidence of the existence of semipermeable membranes around most cells. He believes that that the swelling and the shrinking of plant cells is due to the adsorption or loss of water by the colloids forming the plant cells. One advantage of this point of view is that it eliminates the difficulties which confronted the osmotic pressure theory when it tried to account for the growth of a plant. It has always been a puzzle how salts could be carried through a layer of cells when the membranes were impermeable to these salts by definition. This difficulty disappears with the disappearance of the semipermeable membranes.

Since sodium citrate decreases the absorptive power of gelatine for water, the author concludes that it ought to check oedema, and he actually reduces glaucoma of the eye by injecting sodium citrate solution.

Since fatness is largely a matter of excessive adsorption of water by the tissues, it seemed to the reviewer that sodium citrate should be a cure; but that conclusion is not yet warranted by the facts.

This is an admirable book and reflects great credit on the author. If he continues to turn out scientific work of this grade, we shall all be proud of him.

Wilder D. Bancroft

Der Kautschuk und seine Prüfung. *By F. W. Hinrichsen and K. Memmler. 16 × 23 cm; pp. 263. Leipzig: Verlag von S. Hirzel, 1910. Price: paper, 8 marks; bound, 9 marks.*—The authors discuss the general properties of rubber and then take up the chemical analysis and the mechanical tests. These last two sections are very probably the ones that will interest the rubber chemists the most. Those of us who play with golf balls instead of making them will be more interested in the first section.

The authors discuss: the properties of the latex; the constitution of the hydrocarbons; the other substances in crude rubber; the physical properties of crude rubber; the chemical properties of rubber; the theory of vulcanization; the properties of vulcanized rubber.

The authors have taken into account the articles published in the *Zeitschrift für Kolloidchemie* and have treated the coagulation of the latex and the vulcanization of rubber as problems in colloid chemistry. Their book is consequently the best one on the subject and is indispensable to anybody who is interested in colloid chemistry.

Wilder D. Bancroft

Dynamos and Motors. *A Text-Book for Colleges and Technical Schools. By William Suddards Franklin and William Esty. Direct-Current and Alternating-Current Machines. 14 × 22 cm; pp. viii + 489. New York: The Macmillan Company, 1909. Price: $4.00 net.*—The chemist nowadays has to handle dynamos and motors, and it is consequently essential that he should know something about how they work. He will find this book a very satisfactory one either for reference or for study.

There is a section on general theory and then the subject is discussed under the headings: direct-current generators and motors; elementary theory of alternating currents; alternating current generators and motors; station arrangements and operations. *Wilder D. Bancroft*

Einführung in die technische Elektrochemie. *By Paul Askenasy. Erster Band: Electrothermie. Unter Mitwirkung der Herren R. Amberg, A. Helfenstein, F. Hiller, A. Koenig, G. Leithäuser, B. Neumann, herausgegeben von Paul Askenasy. 15 × 25 cm; pp. 249. Braunschweig: F. Vieweg und Sohn, 1910. Price: paper, 9 marks; bound, 10 marks.*—The volume consists of a series of articles on special topics, each written by an expert in that line. Helfenstein writes on furnaces for calcium carbide and for ferrosilicon; Neumann on iron and steel; Amberg on carborundum and graphite; Askenasy on zinc; Hiller on alundum and carbon bisulphide; Koenig on nitric acid and on ozone.

The volume is good as a whole, though it is uneven. Helfenstein's article on large furnaces for carbide and ferrosilicon is excellent. The articles on carborundum, graphite, alundum, and carbon bisulphide do not seem to represent first-hand knowledge, but are fairly good compilations. The article on nitric acid is not very good and that on ozone is very bad. This last does not give any idea of the real situation. The articles on iron and on zinc are about what would be expected.

While this may sound like faint praise, it should be remembered that there is no book on applied electrochemistry which amounts to anything at all. This is the first attempt by anybody to write a real book on applied electrochemistry and, as such, it has the field to itself. *Wilder D. Bancroft*

Analytische Chemie. *By W. Ostwald. Fifth Edition. 15 × 23 cm; pp. 233. Leipzig: Wilhelm Engelmann, 1910. Price: bound, 8 marks.*—The first edition appeared in 1894; the second in 1897; the third in 1901; the fourth in 1904; and the fifth, the present one, in 1910. The chief difference between this edition and the preceding ones is that we are introduced to phases in the beginning of the first chapter. This is interesting as showing how long it takes even a born teacher like Ostwald to get down to an actual statement of facts as they are. From time immemorial all teachers of chemistry have defined the term 'mixture' in the first session. During that period of time they have always considered a mixture of two pure substances and consequently they have never presented the matter in a general form or in the form based on the student's experiment. Ostwald takes the facts as they are and speaks of a mixture of two phases instead of a mixture of two substances. He then discusses the separation of phases and does not reach the definition of a pure substance until the second

chapter. This may seem like a trifle; but it is not. It is both a revolution and a revelation.

In other respects there is not much change. Methyl orange still poses as a fairly strong acid in defiance of the facts and will probably continue to do so through all future editions. After all, who cares? *Wilder D. Bancroft*

Physical Chemistry. Its Bearing on Biology and Medicine. *By James C. Philip. 14 × 20 cm; vi + 312 pp. New York: Longmans, Green & Co., 1910. $2.10.*—This is chiefly an elementary physical chemistry with no special characteristics. The best thing about it is that the author does state some of the difficulties. Thus, on p. 66, we read that "evidence has, however, been brought forward showing that an individual plant may in certain cases be able to vary its internal osmotic pressure according to that of the surrounding medium."

"Again (p. 84), there is a very striking fact that the inorganic constituents of the blood corpuscle are notably different from those of the plasma: the corpuscles fluid is comparatively rich in potassium and phosphate, while the plasma is poor in these, but rich in sodium and chloride. From the fact that the cell receives its nutrient from the external medium, it appears that the membrane cannot be absolutely impermeable to potassium salts, and yet their retention in the cell would seem to be impossible if permeability of the membrane is conceded. We are therefore driven to assume some specific intervention of the living membrane or some special affinity between the cell protoplasm and the potassium salts."

"The value of the plasmolytic method has lately been questioned by Osterhout. In experiments with *Vaucheria* he found that plasmolysis occurred with sodium chloride solution as dilute as 0.0001 N, the addition of calcium chloride however to the sodium chloride solution, although it raises the osmotic pressure, prevents the contraction of the protoplasm from the cell walls. If one molecule of calcium chloride is present for every 100 molecules of sodium chloride, the cells may be immersed in 0.1 N sodium chloride solutions without suffering plasmolysis. It looks therefore as if, in some cases at least, sodium chloride exerts a specific effect on the protoplasm bringing about a contraction which is indistinguishable from plasmolysis caused by purely osmotic action."

Wilder D. Bancroft

Notions fondamentales de Chimie organique. *By Ch. Moureu. Troisème édition, revue et mise au courant des derniers travaux. 14 × 23 cm; pp. 354. Paris: Gauthier-Villars, 1910. Price: paper, 8.50 francs.*—This is intended as a text to be used in connection with a brief introductory course in organic chemistry. Under general theory the author discusses: molecules and atoms; isomerism; homologous series; and stereochemistry. The remaining chapters are entitled: hydrocarbons; oxygen compounds; nitrogen compounds; metallo-organic compounds; heterocyclic compounds. To the reviewer it seems as through it would be desirable either to teach a student less organic chemistry or to give him a good deal more. It is difficult to see how anybody could master the facts as given and know anything except how to pass an examination. As this is the third edition, the book evidently does fill a need. The second edition was reviewed five years ago (10, 586). *Wilder D. Bancroft*

MOLECULAR ATTRACTION AND THE LAW OF GRAVITATION.

BY J. E. MILLS

SOCIETE CHIMIQUE DE FRANCE BIBLIOTHEQUE

General Outline of the Paper

1. The usual idea of molecular attraction.

2. Statement of the recently discovered law governing molecular attraction.

3. The law expresses the relation between the energy added and the distance apart of the molecules.

4. The law is independent of the mass of liquid taken.

5. Tentative deduction of the law governing the molecular attractive force.

6. Further evidence that the molecular attractive force varies inversely as the square of the distance apart of the attracting particles.

7. The law of gravitation applied to molecular attraction.

8. Application of the law of gravitation to the vaporization of a liquid.

9. The numerator of the law governing the molecular attractive force.

10. The law governing the abstraction of molecular attractive energy from the ether.

11. The law governing the abstraction of gravitational energy from the ether.

12. Possible identity of the laws of molecular and gravitational attraction.

13. The difficulties that arise in explaining gravitation.

14. Newton's law of gravitation is not a necessary consequence of the motion of the heavenly bodies.

15. Newton's law of gravitation is not a necessary consequence of the motion of freely falling bodies.

16. Newton's law of gravitation is not a necessary consequence of the motion of bodies retarded during their fall.

17. Direct measurement of the attraction of two masses.
18. Comparison of all of the attractive forces.
19. The nature of mass.
20. Proposed modification of the statement of the law of gravitation.
21. Facts in accord with the suggested changes.
22. Summary.

1. *The usual idea of molecular attraction.*—Newton thought that the force of gravity was exerted by each individual particle of a mass and made the statement: "Gravitatem in corpora universa fieri."[1] It is said that he attempted to apply the law of gravitation to explain chemical affinity and the molecular cohesion to be observed in all liquid and solid bodies, but I have not been able to verify this statement. Certain it is that the subject was investigated later by Helmholtz and Clerk Maxwell and has been discussed by numerous investigators. The conclusion that the two following facts existed proving that gravitation could not be the cause of molecular cohesion seems to have been almost universally accepted. *First:* The molecular cohesion was a far greater force than the gravitational force. *Second:* The sphere of molecular action was small. If the molecular force obeyed the law of gravitation the sphere of molecular action could not remain small but must include the entire mass taken. This is true because the number of the molecules increases as the cube of the distance from a centrally chosen molecule and the gravitational attraction diminishes only as the inverse square of that distance. The fact that the molecular sphere of action is small seemed to demand that the molecular force decrease with the distance at least as rapidly as the inverse fourth power.

The writer desires to point out some recently discovered facts which seem to indicate that the grounds for this conclusion should be very carefully reconsidered.

2. *Statement of the recently discovered law concerning*

[1] Principia, Book III, Prop VII, Coral, 2.

molecular attraction.—In an extended investigation of molecular attraction the writer has proved that the following law holds true for normal non-associated liquids:

$$1. \qquad \frac{L - E_g}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant, or } \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D}).$$

Here L is the heat of vaporization of 1 gram of the liquid, E_g is the energy spent in overcoming the external pressure as the liquid expands to the volume of the saturated vapor. $L - E_g$ is therefore the so-called internal heat of vaporization and is called λ. d and D are the densities of the liquid and saturated vapor respectively at the temperature of the vaporization. The constant given by the equation is called μ'.

I have said that the above law was proved true. I use the word *proved* advisedly. Thirty-eight liquids of very different chemical constitution have been investigated[1] over a very wide range of temperature extending usually from near the freezing point of the liquid to the critical temperature. For thirty of these liquids the very accurate measurements made by Dr. Sydney Young[2] and his co-workers were available. The proof cannot be quoted here. The eighth paper above cited gives a brief summary of the results obtained. I believe the truth of the law is now established beyond question.

Originally the above relation was theoretically derived. The facts prove that the relation is true and its truth is not dependent therefore upon the truth of the theory by which it was derived. Emphasis is laid upon this fact as some seem to ignore the difference and to believe that the conclusions of the writer are based upon theoretical grounds.

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[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132, 594 (1907); 13, 512 (1909); Jour. Am. Chem. Soc., 31, 1099 (1909); Phil. Mag., Oct., 1910. These papers need revision badly. The eighth paper should be read first, then the last two papers mentioned. The remaining papers can then be briefly examined in the order in which they were written, making allowance for some necessary changes.

[2] Sci. Proc. Royal Dublin Soc., 12, 374 (1910).

3. *The law expresses the relation between the energy added and the distance apart of the molecules.* For a mass of liquid of M grams, containing n molecules each of molecular weight m, if v is the volume of the liquid and V the volume of the saturated vapor, and s_1 the distance apart of the molecules of the liquid and s_2 the distance apart of the molecules of the saturated vapor, we have,

$$2. \qquad nm = M,\ v = \frac{nm}{d},\ v = \frac{nm}{D},\ s_1 = \sqrt[3]{\frac{v}{n}},\ s_2 = \sqrt[3]{\frac{V}{n}}.$$

Therefore

$$\sqrt[3]{d} = \sqrt[3]{\frac{nm}{v}} = \frac{\sqrt[3]{nm}}{\sqrt[3]{n}\,s_1} = \frac{\sqrt[3]{m}}{s_1}. \quad \text{Similarly } \sqrt[3]{D} = \frac{\sqrt[3]{m}}{s_2}.$$

The above relations assume (see page 423).

A. That the molecules are evenly distributed throughout the space occupied by them.

B. That the number of molecules does not change.

Substituting the above values of d and D in equation 1 we have

$$3. \qquad \lambda = \mu' \sqrt[3]{m}\left(\frac{1}{s_1} - \frac{1}{s_2}\right).$$

The heat required to change a liquid into its saturated vapor can be directly measured and the energy necessary to overcome the external pressure during the given expansion can be calculated accurately. The internal heat of vaporization must therefore denote the total energy necessary to add to the liquid in order to effect the given change in the distance apart of the particles. Equation 3 expresses therefore the relation between the distance apart of the molecules and the energy which it is necessary to add to them in order to bring about the given change in their distance apart.

4. *The law is independent of the mass of liquid taken.* —It is also an experimentally established fact that the heat of vaporization of M grams of a liquid is just M times as great as the heat of vaporization of 1 gram of the liquid. Moreover the density of the liquid and the density of the saturated vapor at a certain temperature and pressure are likewise

independent of the number of grams of liquid taken. Consequently we can combine the newly discovered law governing molecular attraction with this fact and write,

$$4. \qquad M\lambda = M\mu'(\sqrt[3]{d} - \sqrt[3]{D}).$$

$$5. \qquad M\lambda = M\mu'^3\sqrt{m}\left(\frac{1}{s_1} - \frac{1}{s_2}\right).$$

5. *Tentative deduction of the law governing the molecular attractive force.* It is well known that the total energy required for any change is dependent only upon the force overcome, and the distance through which the force is overcome, and is quite independent of the method or mechanism of the change. Denoting the energy by E, the force by f, and the distance by s, we have,

$$6. \qquad E = \int f.ds.$$

In the expansion of a liquid the molecular attractive force of any molecule extends doubtless in various directions and to numerous molecules situated at different distances. In determining the total energy required for any given change in volume the action of every molecule upon every other molecule (at least within the molecular sphere of action) must be included in the summation. In order to avoid introducing any assumptions no attempt is made at present to unwind this tangle of individual molecular forces. But it is clear that if the action be viewed as a whole and the summation as regards distance be taken between the limits cs_1 and cs_2 that the force must follow the law:

$$7. \qquad f = -\frac{M\mu'^3\sqrt{m}\,c}{s^2},$$

so that since $^1/_2$ the mass only is moved,

$$8. \qquad M\lambda = E = -\int_{cs_2}^{cs_1} \frac{M\mu'^3\sqrt{m}c}{s^2}.ds = M\mu'^3\sqrt{m}\left(\frac{1}{s_1} - \frac{1}{s_2}\right),$$

as required. It will be noticed at once that for any particular liquid μ' is a constant and $\sqrt[3]{m}$ is a constant. The meaning

of equation 7 is, therefore, that the numerous individual forces acting between the molecules as they expand from the distance apart s_1 to the distance apart s_2 can be replaced by a resultant force acting between the limits cs_1 and cs_2 and this resultant force will vary as $\frac{c\mu'^3\sqrt{m}\,M}{s_2}$. We will denote $c\mu'^3\sqrt{m}$ by μ and write

$$9. \qquad f = \frac{\mu M}{s^2}$$

as a law governing the resultant molecular force.

Equation 9 is deduced and stated as a law governing the *resultant molecular force*. If however M denotes any mass of liquid M might be taken equal to the mass of a molecule m. c would become equal to 1 and the molecular force proceeding from the individual molecule would therefore be

$$10. \qquad f = \frac{\mu m}{s^2} = \frac{\text{Constant}}{s^2},$$

the constant varying with different substances. Since the proof of the fundamental equation 4 (or 5) has been obtained only for molecules in bulk this extrapolation of equation 9 is open to some doubt. The reasonableness of the deduction will however appear later.

6. *Further evidence that the molecular attractive force varies inversely as the square of the distance apart of the attracting partic es.*—Surface action under ordinary circumstances can be disregarded and the heat of vaporization is therefore independent of the shape of the containing vessels. (This fact is in itself significant. It is not due, as has been supposed, to an inverse fourth power law of the molecular attraction but to the mutual absorption of the attraction by the attracted particles. At least I believe the facts later cited warrant this statement. Whatever the explanation, *the fact is* that the shape of the containing vessels can be d s-regarded). It is therefore physically possible and mathematically convenient to have the liquid spherical in shape and to make it expand to a larger sphere in changing to its

saturated vapor. To further simplify the treatment we will assume:

A. *That the molecules are evenly distributed throughout the space occupied by them.*—This assumption is probably always more or less untrue. But if the molecules are shifted from their ideal position by reason of the attractive force, the particles would gain in kinetic energy exactly so much as they would lose in potential energy. We may therefore, without error, consider them to be shifted back into their position of even distribution.

B. *That the number of molecules does not change.*—Except for associated substances or substances undergoing decomposition, it is generally believed, and the belief rests upon considerable experimental evidence, that the number of molecules in the liquid and in the gaseous condition are the same. The equation is not true where this condition is violated.

While I have called the foregoing statements *assumptions* they are really more in the nature of *limitations* and do not seriously detract from the strictness of the proof to follow. Thus even if statement A is not true the subsequent proof will hold provided the term "distance apart of the molecules" is understood to mean their *average* distance apart. Statement B limits the application of the proof to chemically stable non-associated liquids.

Under these conditions if s_1 is the average distance apart of the molecules of the liquid and s_2 the average distance apart of the molecules of the vapor, it is readily seen from the symmetry of the figure that if any molecule is distant xs_1 before expansion, after expansion it will be distant xs_2. And a little consideration will show clearly that in integrating equation 6 we are summing up a large number of individual actions each of exactly the same character and each represented by

$$11. \qquad E = \int_{xs_2}^{xs_1} f.\,ds,$$

x being a constant during each integration but varying in

value for every individual integration. Since x is a constant during each integration and the law of the force remains the same during all of the integrations, it is possible to replace all of the $n^2 - n$ different x's by their sum, which we will call c and perform but one integration. Therefore the law of the molecular attractive force must be

$$12. \qquad f = -\frac{M\mu'^3\sqrt{m}\,c}{s^2},$$

so that

$$13. \qquad Mx = \int_{cs_2}^{cs_1} \frac{M\mu'^3\sqrt{m}\,c}{s^3}\,ds = M\mu'^3\sqrt{m}\left(\frac{1}{s_1} - \frac{1}{s_2}\right).$$

c can hardly be considered a function of the distance apart of the molecules, but is apparently a function of the number within the sphere of molecular action. *If c is not a function of the distance apart of the molecules the force between the molecules must vary inversely as the square of their distance apart in order to produce the observed law.*

From the point of view of the writer c is dependent on the absorption or neutralization of the "lines of force" proceeding from a molecule. The sum total of these is always a constant and the distance at which they are neutralized is proportional to the distance apart of the molecules. c becomes therefore a constant for any particular substance.

The idea that the force of molecular attraction *cannot* vary inversely as the square of the distance apart of the attracting particles is so universal that I stop here to lay an added emphasis on the above proof. The molecular attraction *can* vary inversely as the square of the distance apart of the attracting particles. The idea that the inverse square law of the distance is impossible for molecular forces is founded on the error that the forces must vary as the product of the masses of the attracting particles.

I would also call attention to the fact that I am not now trying to explain *why* the inverse square law of the molecular attraction is true. I have purposely so far said nothing about the mechanism of the action. If some one supposes

that the inverse square law is due to the mutual action of positive and negative forces emanating from a molecule each varying as the inverse fourth power of the distance, the supposition need not, so far as I can see, *necessarily* contradict the inverse square law. If the final explanation of the inverse square law proves to be connected with the fact that Descartes' idea that the *total quantity of motion* in the *universe* (including the ether which Leibnitz and modern science failed to include) is a constant, my present statements are not to be taken as contradictory of such an explanation. I am simply using the nomenclature at present adopted to express a fact. The explanation of the fact I am not just here discussing.

Some one may also be troubled by a possibility already noted by the writer in a previous paper, namely, that it is not *certain*, that the energy *per se* of a molecule in the liquid condition is equal to the energy of a molecule of its own vapor at the same temperature and under the same pressure. Therefore it is possible that some of the energy needed for overcoming the molecular attraction during the vaporization of a liquid is drawn from the liquid itself. There is certainly this possibility, and it should be carefully borne in mind that the laws that I am considering in this paper deal with the *energy which it is necessary to add to a liquid during its vaporization and with the corresponding force exerted throughout the molecular distances conditioned by the vaporization.* The possibility of an internal source of energy therefore in no degree lessens the finality of the conclusions *as made.* I might add also that such a concealed source of energy could hardly escape detection unless it followed a law similar to the one under discussion.

7. *The law of gravitation applied to molecular attraction.*— The amount of energy that would be required to effect a given expansion if the molecular attraction obeyed the law of gravitation can be readily found. Helmholtz in 1854 investigated the amount of energy that would be given out by the contraction of the sun in order to determine if the energy

continually radiated from that body could be thus obtained. In this investigation he assumed that the particles of which the sun was composed were at the same temperature before as after the contraction, the excess of energy having been radiated off into space. He also assumed that the force acting between the particles of the sun's mass obeyed the Newtonian law of gravitation. Hence the investigation was essentially the same as the one at present desired. In order to make possible a better mathematical treatment Helmholtz assumed that the sun was homogeneous in density. Helmholtz[1] found that the total heat, W, given out by the contraction of a homogeneous sphere from radius CR_o to R_o under the influence of a force, $f = \frac{K^2(dM)^2}{s^2}$, between the elements ($dM$) of the mass, was equal to

$$17. \qquad W = {}^3/_5 K^2 \left(\frac{1}{R_o} - \frac{1}{CR_o}\right) M_o{}^2,$$

where M_o is the total mass of the sphere.

In applying the above investigation as given by Helmholtz to the contraction of the saturated vapor into the condition of the liquid it is to be noted that since the volume of a sphere, ${}^4/_3 \pi r^3$, is equal to its mass divided by its density we have, $CR_o = \sqrt[3]{\frac{3M}{4\pi D}}$, and $R_o = \sqrt[3]{\frac{3M}{4\pi d}}$. Also during the contraction of the saturated vapor to the volume of the liquid the total work done against the attractive forces is equal to $M(L - E_g) = M\lambda = W$. Therefore substituting these values in equation 17 we obtain

$$18. \qquad M(L - E_g) = M\lambda = W = 0.9682\, K^2\, M^{5/3}(\sqrt[3]{d} - \sqrt[3]{D}).$$

It should be noted that the actual value of this constant as well as the constant of equation 25 depends upon the original assumption of Helmholtz that the sphere was *uniform in density*. I do not see how the transformation from a

[1] See Moulton's "Celestial Mechanics," page 58, or Jour. Phys. Chem., 11, 147 (1907).

sphere of uniform density to one of uniformly distributed particles could effect any change in the nature of the energy relations involved.

So long as a *constant mass is taken* equation 18 will reduce to the form of equation 1, namely $\frac{L-E_s}{\sqrt[3]{d}-\sqrt[3]{D}}=\text{constant}$. If, however, the *mass is varied*, equation 18 informs us that acting under the law of gravitation the work done should vary as the 5/3 power of the mass. It should require 3.2 times as much heat to vaporize 2 grams of liquid as to vaporize 1 gram. As a matter of fact, we know that it requires only twice as much heat to vaporize 2 grams as to vaporize 1 gram.

8. *Application of the law of gravitation to the vaporization of a liquid.*—It is interesting to take the equation derived by Helmholtz for calculating the energy given out by the contraction of the sun under the action of gravitational force, and by changing the constant, apply the equation to the contraction of a saturated vapor into the condition of a liquid. For the purpose of illustration isopentane is chosen. In Table 1 below is given for isopentane the density of liquid and saturated vapor[1] and also the internal heat of vaporization of 1 gram.[2] The equation of Helmholtz has been shown to reduce to the form given in equation 18. If 0.9682 K^2 be taken equal to 105.46, and 1 gram of liquid is used, equation 18 reduces to the yet simpler form,

19. $$W = 105.46\,(\sqrt[3]{d}-\sqrt[3]{D})\text{ calories.}$$

I give below in Table 1 under the heading "W" the values obtained from equation 19. Similar comparisons are given for ether and for benzol using for the constants 103.76 and 109.26 respectively. It is inconceivable to me that the agreement between W and $L-E_E$ could be accidental. A full investigation of equation 19 for the thirty-eight substances examined is given in *J. Am. Chem. Soc.*, 31, 1099 (1909).

[1] Sci. Proc. Roy. Dublin Soc., 12, 374 (1910).
[2] Jour. Am. Chem. Soc., 31, 1099 (1909).

TABLE I

Isopentane						Ether			Benzol		
Temperature	Density of liquid d	Density of vapor D	$\sqrt[4]{d} - \sqrt[4]{D}$	W	$L - E_E$	Temperature	W	$L - E_E$	Temperature	W	$L - E_E$
0° C	0.6392	0.001090	0.7585	80.0	81.3	0°	84.0	85.4	0°	100.0	99.2
20	0.6196	0.002344	0.7197	75.9	75.7	20	79.9	80.0	80	86.7	86.7
40	0.5988	0.004456	0.6783	71.5	71.1	40	75.5	75.0	100	82.8	82.4
60	0.5769	0.007837	0.6339	66.8	66.2	60	71.0	70.4	120	78.5	77.4
80	0.5540	0.01287	0.5869	61.9	61.6	80	66.0	65.4	140	74.1	73.4
100	0.5278	0.02020	0.5357	56.5	56.7	100	60.5	60.4	160	69.5	69.5
120	0.4991	0.03106	0.4788	50.5	50.9	120	54.3	54.5	180	64.7	65.2
140	0.4642	0.04728	0.4127	43.5	44.0	140	47.5	48.1	200	59.2	59.7
160	0.4206	0.07289	0.3316	35.0	35.4	160	39.5	39.8	220	53.1	53.8
180	0.3498	0.1258	0.2035	21.4	21.0	180	27.9	27.4	240	46.0	46.5
185	0.3142	0.1574	0.1399	14.7	14.0	190	17.7	16.6	260	37.2	37.6
187	0.2857	0.1833	0.0905	9.5	8.9	193	10.9	9.7	280	23.7	23.4
187.4	0.2761	0.1951	0.0712	7.5	6.9	193.8	0	0	288.5	0	0
187.8	0.2343	0.2343	0	0	0						

The formula used by Helmholtz to represent the energy given out by the contraction of the sun does, by changing the constant and keeping the mass of liquid constant, represent the energy given out by the contraction of isopentane from the gaseous to the liquid condition. And not only isopentane but essentially as well all of the non-associated liquids examined, for similar comparisons for all of these substances have already been published. I have here republished the results for isopentane, ether, and benzene, as coming from Helmholtz's formula only to emphasize the statement that I do not go beyond the facts when I declare that, ***as regards variation with the distance, the law of molecular attraction is identical with the law of gravitation, and precisely the same formula is applicable to both.***

9. *The numerator of the law governing the molecular force.* —The facts to be noted are as follows:

1. The gravitational law of force is $f = K\frac{MM'}{s^2} = \frac{KM^2}{s^2}$. This law used to calculate the energy given out on the contraction of molecules leads to an equation of the form, energy $= cM^{5/3}(\sqrt[3]{d} - \sqrt[3]{D})$.

2. The equation actually governing the energy given out on the contraction of molecules is: energy $= M\lambda = \mu' M(\sqrt[3]{d} - \sqrt[3]{D})$. As before noted, this equation, if universally true, indicates that for the molecular force, $f = \frac{\mu m}{s^2}$.

3. If a constant mass is taken and the constant suitably altered, the gravitational law, energy $= c\ M^{5/3}(\sqrt[3]{d} - \sqrt[3]{D})$, becomes identical with the molecular law, $M\lambda = \mu' M(\sqrt[3]{d} - \sqrt[3]{D})$.

4. The molecular sphere of action is small. The gravitational law of the force would make the molecular sphere of action include the entire mass taken.

5. Every molecule is subject to the action of attractive forces and itself exerts an attractive force and the attraction between the molecules is therefore of a mutual character.

Considering first the meaning of the expression for the

molecular force, $\frac{\mu m}{s^2}$, it will be seen that μ is a constant for any particular substance, and m is likewise a constant for any particular particle, and therefore for any molecule, $f = \frac{\text{constant}}{s^2}$. The molecular force radiating or proceeding from a molecule is not therefore increased by increasing the number of surrounding molecules. The sum total of the force of a molecule at a given distance is a constant, and if so much of the force is used up in attracting other molecules there remains an exactly equivalent amount less of the force. *Molecular force can therefore be viewed as an attribute of the molecule* in exactly the same way that chemical force is an attribute of the atom. Just as the chemical force is used up (absorbed or neutralized) by a combination of one atom with another so the force of molecular attraction is absorbed or neutralized by the surrounding molecules. An atom of sodium has a certain amount of "chemical affinity" and an atom of chlorine has a certain amount of "chemical affinity." When these combine the active affinity of each disappears and the sodium cannot continue to attract other chlorine atoms or the chlorine to attract other sodium atoms. The attraction of the combined sodium and chlorine can be regarded as absorbed, neutralized, destroyed, or shielded (the word used makes little difference, seeing that the mechanism of the action is not understood) from other sodium and chlorine atoms. The sphere of action of the chemical force is very small although the force of "chemical affinity" is very great. The absorption of the molecular attraction by the attracted particles in the same way makes the sphere of molecular action small, even though the inverse square law is obeyed by the molecular force so long as its power is operative.

Again, the total molecular force varies as a constant times the mass. The constant depends upon the *nature* of the substance and remains the same constant however much of the substance is taken. The mass is a constant property

of every molecule of a particular substance but *varies with the number of molecules*, that is with the mass, taken.

The foregoing discussion of the law of the molecular force proposed has shown that the law very readily explains the facts noted under the headings 3, 4, and 5, above. It only remains to show that the complex molecular interaction can now be considered and that the fundamental equation can be rigidly deduced from the law of force given provided we assume:

C. *That the attraction of any molecule is absorbed at a distance proportional to the distance apart of the molecules.*—Since the direction of the force is mathematically a matter of no concern we can regard all of the attractive force of one molecule as concentrated upon another molecule at distance cs_1. After expansion this molecule is distant cs_2 and the energy required for the expansion is

$$20. \qquad \int_{cs_2}^{cs_1} -\frac{\mu' m^3 \sqrt{m}\, c}{s^2}\, ds = \frac{\mu' mc^3 \sqrt{m}}{c}\left(\frac{1}{s_1} - \frac{1}{s^2}\right).$$

To pull n molecules from each other the total energy is simply n times as great and we have therefore for the total energy, M λ, required to overcome the molecular attraction in vaporizing a mass of liquid M, containing n molecules, each of molecular weight m,

$$21. \qquad M\lambda = \mu' n m^3 \sqrt{m}\left(\frac{1}{s_1} - \frac{1}{s_2}\right).$$

Substituting the values given in equation 2 this equation reduces readily to the form

$$22. \qquad M\lambda = M\mu'(\sqrt[3]{d} - \sqrt[3]{D}).$$

In conclusion therefore, I think that there can be but little doubt that the molecular attraction follows the law,

$$23. \qquad f = \frac{c\mu' \sqrt[3]{m}\, m}{s^2} = \frac{\mu m}{s^2}.$$

10. *The law governing the surrender of energy from the ether.*—Taking into consideration the fundamental nature

of the attractive forces it is certainly probable that equation 1, $\lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D})$, will represent under all circumstances, the temperature remaining constant during the expansion, the work done against the force of molecular attraction in moving molecules further apart. Now the further the molecules are moved apart the less becomes the value of D, and D will finally become zero when the molecules have been moved an infinite distance apart. Making, therefore, D equal to zero, and remembering that the density, d, is equal to $\sqrt[3]{m}/s$ we can write:

24. $\lambda_\infty s$ = constant (For M grams the constant is $M\mu'\sqrt[3]{m}$) as the very simple form for the law under discussion. This statement means simply this:

In any normal substance the internal heat given out as the molecules approach each other, multiplied by the distance apart of the molecules, is equal to a constant. The significance of this statement is very great. The potential energy of molecular attraction, since it does not reside in the particles themselves, must reside in the medium surrounding the particles, that is in the ether. (See under heading 18.) Potential energy of attraction is therefore energy due to the position of attracting particles of matter in the ether, and *the potential energy of attraction is a property of the ether. The above law therefore governs the surrender of molecular attractive energy from the ether.*

11. *The law governing the surrender of gravitational energy from the ether.*—The law governing the abstraction of gravitational energy from the ether can likewise be put into a very simple form. Taking equation 17 and making CR_o infinite, we have for the energy, E_∞, given out on the contraction of the mass from an infinite distance, since

$$R_o = \sqrt[3]{\frac{3M}{4\pi m}}\, s = \sqrt[3]{\frac{3m}{4\pi}}\, s.$$

25. $E_\infty\ s$ = constant. For M grams the constant is $0.9682\ K^2M^{5/3}\sqrt[3]{m}$ or

$$\frac{0.9682\ K^2M^2}{\sqrt[3]{n}},$$

where n is the number of molecules in the mass taken. (See also the remark after equation 18.)

Comparing equation 24 with equation 25 it will be seen that for any given mass the law governing the surrender of molecular attractive energy from the ether is of precisely the same form as the law governing the surrender of gravitational attractive energy from the ether. The only difference is in the constant involved and this difference depends upon the mass taken.

12. *Possible identity of the laws of molecular and of gravitational attraction.*—The evidence advanced has pointed clearly and almost conclusively to the belief that the three following laws governing molecular attraction and energy changes caused by that attraction are true.

(*a*) $f = \frac{\mu m}{s^2}$, where f is the molecular force.

(*b*) $\lambda_\infty s$ = constant = $\mu' \sqrt[3]{m}\, \mathrm{M}$, where λ_∞ is the internal energy given out on the coming together of the molecules from an infinite distance to distance s.

(*c*) $\mathrm{M}\lambda = \mathrm{M}\mu'(\sqrt[3]{d} - \sqrt[3]{\mathrm{D}})$—the fundamental law as experimentally proved.

The usual ideas concerning gravitational attraction lead to the following corresponding laws for that force:

(a') $f = \mathrm{K}^2\frac{\mathrm{MM}'}{s^2} = \mathrm{K}^2\frac{\mathrm{M}^2}{s^2}$ for homogeneous substances.

(b') $\mathrm{E}_\infty s$ = constant = $0.9682\ \mathrm{K}^2\mathrm{M}^{5/3}\sqrt[3]{m} = \frac{0.9682\ \mathrm{K}^2\mathrm{M}^3}{\sqrt[3]{n}}$.

(c') $\mathrm{E} = 0.9682\mathrm{K}^2\mathrm{M}^{5/3}(\sqrt[3]{d} - \sqrt[3]{\mathrm{D}})$.

The similarity of these laws—they are identical except for the mass and the constant involved—must make one pause and think and *think again*. *Are not the laws really identical?* Is not the difference due to some misconception or misconstruction on our own part? Notice that a drop of liquid under the action of molecular forces arranges itself into a sphere. The radius of the sphere may be many thousands of times greater than the radius of the so-called "sphere of molecular action." Notice that the earth also and the

planets under the action of the gravitational force assume a spherical form, except in so far as modified by their rotational movements. Was not the earth at one time merely a large drop of liquid and was not its shape determined by the same law that determined the shape of the smaller drop?

The gravitational attraction applies to every mass and to every measurable particle of every mass, in the universe. Is it possible that the mere subdivision of this mass into molecules should alter the *nature* of the law? The molecular attraction applies to every molecule in the universe. Is that law altered by the collection of the molecules into an appreciable mass? Would the contraction of a sun made of isopentane differ as regards the *nature of the laws concerned* from the contraction of a few grams of isopentane in the laboratory? Are there in reality two forces with laws almost, but not quite identical, which apply to the one operation—the aggregation of matter? The idea is not reasonable and *there is but little evidence for it.*

If the two forces, gravitational and molecular, are identical, which law of force above given is the correct law? *I think that the statement of the law of gravitational force as made by Newton needs some modification and that it is possible to bring the law of molecular and gravitational force into harmony with the facts and with each other.*

I only ask that the statement made be judged by the evidence that is, or that can be, presented. It should, at the outset, be understood clearly that the gravitational law as expressed by Newton and commonly interpreted since his day, cannot, unmodified, be made to apply to molecular attraction for the following reasons:

1. The sphere of molecular action would not be small and the liquid could not be regarded as homogeneous throughout.

2. The heat of vaporization of a liquid would not vary as the mass of the liquid taken.

3. The boiling point of a liquid would vary with the amount of liquid taken and with the shape of the vessel.

4. Surface tension phenomena generally would vary with the amount of liquid and the shape of the vessel.

5. The gravitational force as calculated for molecular distances by Newton's law is not great enough to account for the observed phenomena of cohesion.

It should be further remembered that since Newton in 1682 deduced the law of gravitation, all of the attempts—and they have been numerous—to formulate a sufficient cause for the law have completely failed. The attempts have ended not alone in failure to formulate a cause for the law, but in emphasizing, most distinctly, the difficulty of forming such a conception at all. May not the real cause of the trouble lie in the fact that scientists have been trying to explain how a force can be infinitely multiplied and absolutely unaffected by intervening matter, when force with such properties has really no existence? The whole situation merits careful consideration.

13. *The difficulties that arise in explaining gravitation.*—The difficulties that arise in attempting to explain gravitational force (as that force was understood by Newton and by scientists since his day) have been most excellently summarized by W. B. Taylor,[1] and only the unusual length of this paper prevents my quoting his statement of the "Conditions of the Problem" in full. Without reviewing the entire discussion I would place additional emphasis on three facts required by the usually accepted laws of gravitation.

First.—The attraction exerted by a particle can be infinitely multiplied merely by the introduction of other particles. If by some act of creation new particles come into existence the former attraction of every particle in the universe is thereby increased. *Is it not unreasonable to suppose that a particle could exert its attractive pull upon one thousand, or one million, or one hundred million, particles and yet always*

[1] "Kinetic Theories of Gravitation," Smithsonian report, 1876. The entire paper should be read by those interested in the cause of gravitational force.

have just as much of its force remaining to exert on other particles brought within the same distance?

Second.—A particle at the center of the earth attracts a particle at the surface of the earth, or a particle at the center of the sun *exactly as if there were no intervening matter. Is it reasonable that the introduction of particles of matter into the space surrounding a molecule should be absolutely without influence on the wave motion or emanation (or more spiritual essence) which acts as if it proceeds from the molecule and gives rise to the phenomena of attraction? And that this filling in of the space surrounding a molecule with other particles of matter (or centers of energy, if you choose) should be able to continue, ad infinitum, without disturbing the attractive radiation proceeding from the body?*

Third.—The attraction is propagated supposedly with an instantaneous velocity, but with a proved velocity[1] at least 50,000,000 times that of light; that is, the proof holds unless there is some unknown compensating action.

To the reader these difficulties may well appear insurmountable. They have proved equally as insurmountable to every student of the subject. Newton, himself, in his oft-quoted third letter to Bentley, dated Feb. 25, 1692–3, stated: "That gravity should be innate, inherent, and essential to matter, so that one body may act upon another at a distance, through a vacuum, without the mediation of anything else, by and through which their action and force may be conveyed from one to another, is to me so great an absurdity, that I believe no man who has in philosophical matters a competent faculty of thinking can ever fall into it. Gravity must be caused by an agent acting continuously according to certain laws; but whether this agent be material or immaterial, I have left to the consideration of my readers."

Twenty-five years later, "as if driven back from every assault to the only retreat, which in earlier years he had stigmatized as 'so great an absurdity' that no competent thinker could 'ever fall into it,' he despairingly asks: 'Have

[1] Taylor: "Kinetic Theories of Gravitation."

not the small particles of bodies certain powers, virtues, or forces, by which *they act at a distance*.....What I call "attraction" may be performed by impulse, or by some other means unknown to me. I use that word here to signify only in general any force by which bodies tend toward one another, whatsoever be the cause.' And beyond this point, no human research has yet been able to penetrate."[1]

There is no need to review the fruitless effort expended in trying to get an explanation of the gravitational law since the time of Newton. Faraday[2] clearly and repeatedly asserted his belief that no force with the properties usually ascribed to gravitation could exist. The question of the truth of the gravitational law cannot be finally settled by an appeal to our minds as to the relative difficulty or ease of the conception, though such an appeal is not without value. Let us proceed further to examine in detail the evidence for the law.

14. *Newton's law of gravitation is not a necessary consequence of the motion of the heavenly bodies.*—Kepler deduced from the observations of Tycho Brahe and his own three empirical laws governing the motion of the planets about the sun.

Newton perceived that these motions of the planets about the sun and the motion of the moon might be determined by the action of a force differing in no substantial respect from the force of gravity as exhibited on the earth. He investigated this brilliant conception and finally stated the universal law of gravitation as causing the observed planetary motions, $g = k\frac{MM'}{s^2}$.

Newton did not know the mass of the earth, or of the moon, or of the sun, or planets. He could not therefore prove the numerator factor of his law correct so far as the masses of the heavenly bodies are concerned, and we are to-day as totally without proof. All of Kepler's laws follow on the assumption of a central acceleration varying inversely as the square of the

[1] Taylor: "Kinetic Theories of Gravitation," page 5.

[2] "Essay on the Conservation of Forces," and other writings.

distance from the center. The fact that this central acceleration varies as the product of the masses of the attracting bodies was a pure assumption, so far as the heavenly bodies are concerned, made because Newton saw clearly that all masses appeared to be concerned in such mutual attractions.

The mass of the earth was really determined for the first time by Maskelyne in 1774 who weighed the earth against a mountain (by measuring the deflection of a plumb-line) and obtained its weight on the assumption that the law of gravitation as stated by Newton was true. Since that time various investigators have made use of four methods for determining the mass of the earth but in all of these methods the truth of Newton's law of gravitation *is assumed*. Really only the attraction or acceleration between various masses is directly determined and the mass is calculated on the assumption that Newton's law of gravitation is correct.

When we consider the various methods of obtaining the masses of the other heavenly bodies we find always a similar condition. The relative amount of the attractions are determined and the masses are calculated on the basis of Newton's law. *Astronomical data gives absolutely no evidence to show that gravitational attraction varies as the product of the masses of the attracting bodies.* It does prove that a force of a definite and apparently unchanging magnitude emanates as if from the center of each heavenly body within the limit of investigation and that this force varies inversely as the square of the distance from its origin. The magnitude of the force exerted depends upon some property of the body.

Astronomical data does *apparently* further prove that this force of gravity cannot be shielded, or refracted, and that its action is instantaneous throughout all ascertained distances. Thus the passage of the moon between the sun and the earth does not alter in the slightest degree the relative motion of the sun and the earth and therefore apparently does not disturb the attraction which exists between them. This remarkable circumstance (equally true for all similar cases) has doubtless kept many from questioning the truth

of Newton's statement of the gravitational law. An explanation of the actually observed facts is suggested later.

15. *Newton's law of gravitation is not a necessary consequence of the motion of freely falling bodies.*—If bodies, initially at rest near the earth's surface, fall freely towards the earth under the influence of the gravitational attraction the following laws apply: Let v = velocity acquired, a = acceleration produced by gravity, t = time, s = distance traversed. Then,

26. $$v = at;\ d = \frac{at^2}{2};\ as = \frac{v^2}{2}.$$

These laws and these laws alone are sufficient to determine the motion of bodies near the earth free to fall under the action of gravitational attraction. Motion on an inclined plane and the motion of pendulums can be regarded as falling under this head. It should be noticed particularly that the mass of the body nowhere enters into thee quations. That is to say a feather, a gram of aluminum, and a pound of lead, in a vacuum, all fall at exactly the same rate, and that rate is in no sense dependent upon their relative mass. *It should be borne in mind that if during its fall the mass of the lead were altered to that of the aluminum, or to that of the feather, the change of mass could not be detected by any observation upon the motion of the lead.*[1] It is therefore perfectly clear that no observation of the motion of a body falling freely towards the earth will give any evidence as to the *mass* of the body. This statement as has already been shown applies also to the motion of the heavenly bodies.

[1] Objection has been raised to this statement on the ground that the alteration of mass is a purely hypothetical question and also on the ground that the conservation of energy must be considered. I do not believe that the alteration of the mass is a purely hypothetical question. I suspect very strongly that it does actually take place and I am here giving one reason why we have heretofore failed to detect it. As regards the conservation of energy, if the kinetic energy of a body is due to its motion, my very point is that this motion is not changed. If as I think more likely the kinetic energy of a moving body is more or less a property of the ether surrounding the body then the energy is adjusted when the ether condition is adjusted—that is probably completely only when the system becomes static.

Newton's calculation showing that the moon "fell" towards the earth required no knowledge of the *mass* of the moon or of the earth. It did prove that the earth's attraction extended to the moon and that this attraction varied inversely as the square of the distance from the center of the earth. A cannon ball at the distance of the moon once given the velocity of the moon would follow its orbit very nearly. The difference observed would be due to the fact that the moon and the earth revolve around their common center of gravity which would be changed by the substitution of the cannon ball for the moon. Now *on the supposition of Newton's law of gravitation the relative mass* of the moon and earth can be obtained from this fact. Similarly the relative mass of the planets is obtained from the divergence from Kepler's third law. It is thus a little curious that our knowledge of the relative masses of the heavenly bodies is largely due to their divergence from the very laws Newton's law was advanced to explain. The divergence of course likewise takes place in accordance with Newton's law.

16. *Newton's law of gravitation is not a necessary consequence of the motion of bodies retarded during their fall.*—Imagine two equal masses of say 99 grams each connected by a cord and balanced by passing the cord over a nearly frictionless pulley free to revolve. Now motion in such a system can be started by placing a small rider, let us say of 2 grams, upon one of the masses. The mass will descend under the action of the gravitative force exerted by the earth upon the mass of 2 grams. The velocity acquired will however be only 1/100 of the velocity acquired by the 2-gram mass if it be allowed to fall freely. And in general, *it can be thus shown that the force of gravity is proportional to the mass of the attracted body.* The same fact may also be demonstrated by measuring the gravitational attraction upon any body and then determining the inertia of the body when it is subjected to motion in a horizontal plane. Always *the force of gravity appears to be proportional to the inertia of the body.* But this fact, so far from constituting a proof of Newton's law of

gravitation, is a proof only of the law of molecular force given, namely, force $= \frac{\text{constant} \times \text{mass}}{s^2}$.

17. *Direct measurement of the attraction of two masses.*— When Newton proposed his magnificent generalization he had *no proof whatever* that the gravitational attraction did vary as the product of the masses of the attracting bodies. The attraction of two bodies, the masses of which could be independently determined, was not measured by any experimenter for nearly a hundred years after the law had been proposed. Newton saw that the attraction of gravity apparently extended to all bodies, that it apparently could not be shielded, deflected, or absorbed in any way, and that the earth's attraction, at least for bodies near the earth, varied as the mass of the bodies. From these facts Newton made his generalization.

In attempting to find the constant of gravitational attraction the attraction of two masses has been directly measured by a number of experimenters using several different methods. The experiments are difficult in the highest degree and naturally the results did not at first agree well with each other. But the difficulties have been gradually overcome and reliable measurements have now been made of the attraction of two masses at known distances under circumstances permitting of the elimination of the numerous disturbing elements. The fact that these experiments were performed under diverse conditions, with masses of varying size and substances, at varying distances, and yet give agreeing (considering the difficulty of making accurately the measurements involved) values for the gravitational constant k, constitutes the sole *proof* existing to-day, so far as the writer is aware, of the truth of Newton's statement that substances universally attract as the *product of their masses.* The proof that has thus accumulated cannot be lightly put aside. An interesting account of these experiments is to be found in "The Laws of Gravitation," by A. S. Mackenzie.

The agreement shown by these experiments is one fact

that must be explained in explaining gravitation. I will refer to these experiments later.

18. *Comparison of all of the attractive forces.*—The nature of the gravitational and of the molecular attraction is a very fundamental question. The nature of matter, of inertia or mass, the nature of the other attractive forces, and the nature of the ether must all be considered to some extent at the same time. The table below gives the usually accepted belief as to the action of the attractive forces. The general resemblance between these forces is so striking, I think, as to warrant a very serious consideration of any idea which leads to the belief that all of the forces do not follow the same law. Are they not perhaps all, in fact, one and the same force? Are not the apparent exceptions to a complete similarity between the action of the forces due to our lack of knowledge, or to a wrong understanding and interpretation of the facts involved? In seeking an answer to these questions the interpretations suggested below of certain facts are new, and in order to prevent confusion a general discussion of the table precedes the more detailed consideration of the facts.

All of the attractive forces appear to proceed from some particle or mass of matter as a center and to be exerted upon some other particle or mass of matter across an intervening space which is supposed to contain ether. Thus always in the action of the attractive force at least two particles are concerned and these two particles possess, because of their mutually attractive force, a so-called potential energy, which can be obtained from the system by causing the particles to approach. Without making any further supposition whatever, fundamental mechanical principles being true, as to the nature of the particles, of the ether, or of the attractive force, it is clear that this potential energy does not reside in the two particles from which the force appears to proceed, for these particles can be supposed at rest and therefore devoid of all energy *per se.* (If when the particles are at rest, they possess internal motion, it can hardly be supposed that the internal motion is changed by their approach. Yet

Comparison of the attractive forces

	The origin of the force	Medium of propagation of the force	Is the amt. of the attraction limited?	Does the force show positive and negative tendencies?	The effect of temperature on the force	Velocity of propagation of the force	Law of variation with the distance	Numerator factor of the force
Interatomic[1] Chemical	Matter	Ether	Yes	Yes	No effect	?	?	Nature of atom & Nature of atom
Molecular	Matter	Ether	Yes	?	No effect	?	$1/s^2$	Nature of molecule & Nature of molecule
Gravitational	Matter	Ether	No	No	No effect	Apparently instantaneous	$1/s^2$	Mass × Mass
Electrical	Matter	Ether	Yes	Yes	?	186000 miles per second	$1/s^2$	Charge × Charge
Magnetic	Matter	Ether	Yes	Yes	?	?	$1/s^2$	Strength of pole × Strength of pole

[1] As evidenced in radium, polonium, etc.

perhaps this possibility should not be regarded as eliminated.) This potential energy, since it does not reside in the particles themselves, must reside in the medium surrounding the particles, that is in the ether. Potential energy of attraction is therefore energy due to the position of attracting particles of matter in the ether, and *the potential energy of attraction is a property of the ether*. This view is pretty generally accepted.

It is equally clear that this energy of the ether exists or exists in an available form, solely on account of the presence of the attracting particles. *The attraction must therefore be caused by some interaction between the attracting particles and the ether.* While two particles and the ether are necessary to the phenomena of attraction, it is quite clear,[1] that the two particles are not necessary for the interaction between the matter and the ether. That is, *each particle alone must interact with the ether in such manner as to produce a modified condition of the ether in its neighborhood.* Two or more "modified conditions" of the ether produce an attraction between the particles causing the "modified conditions," and the attraction is due to some connection between these modified ether conditions. *It is clear that if one particle alone in the ether be considered, the total effect of its interaction with the ether is a proper measure of its potential attractive energy, which under these conditions becomes a constant and definite property of the particle.*

Without knowing, or at present considering, the mechanism of the interaction between the ordinary particle and the ether yet a further conclusion can be drawn. Consider two particles at an infinite distance apart, each particle being surrounded with its modified sphere of ether. Probably these "modified spheres of ether" proceed from a particle somewhat as does light from a central source of light. Under

[1] The author holds the belief that two particles of ordinary matter or of ether cannot exert any action upon each other across an absolutely empty (devoid of matter and of ether) intervening space. To attempt to justify this belief would lead to an examination of the foundations of thought, mathematics, and science. Such an examination would lead us too far from the immediate object of the present paper and cannot be undertaken here.

the influence of their mutual attraction caused by these modified spheres of ether the two particles commence to approach each other and gain in kinetic energy. The ether loses therefore a corresponding amount of energy and must suffer change to a corresponding extent. The loss of this energy by the ether must be to that extent a reversal of the "modified condition of the ether" caused by the particles of matter; for the cause of the attraction, as has been seen, lay in this modified condition of the ether and when the cause produces a change the cause must itself suffer an equal opposite change. If this does not happen there would be a creation of energy. *In fact the modified spheres of ether can be regarded as produced by the interaction between the particles and the ether and as representing so much available energy, and if some of this energy is used up, the amount of energy remaining must be diminished by an exactly equivalent amount.* The attractive force, which is a manifestation of this energy, must be subject to a corresponding limit. That is, *the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.*

Strenuous objection has been raised to this sentence and I have been accused of confusing force and energy. I am not confusing the two. I think force in its last analysis has to do with the quantity of motion transferred per unit of time. I do not consider this idea of force heretical. When the *totality of a force* is considered per unit of time (as is here done) it will be seen that the quantity of motion transferred can be increased only by increasing the velocity of the moving particles or by altering their distance apart (or their number per unit of volume, which is the same thing). Both of these operations (alteration of velocity or distance apart) would require the expenditure of additional energy. Where the energy is fixed and a definite system is considered the total

force is also constant. I have been cited to the hydraulic press, etc., as illustrations of how force can be multiplied. The total force in a hydraulic press has to do with the total motion exchanged among the molecules of the liquid used. For a given press the *total force of the system is constant* unless the amount of liquid used, the temperature of the liquid, or the distance apart of the molecules are altered, and *all of these alterations require the expenditure of energy.* When we keep the conditions in the press the same the force exerted at one end is multiplied at the other because we consider only a part of the total force and that part as acting on different areas. There can really be no multiplication of the total force except as above stated. I see no reason whatever for attributing "powers" to a molecule which are not possessed by any mechanism whose real nature we are able to understand. The disturbance set up by the interaction of a molecule and the ether is in my opinion perfectly definite in amount for a given condition of the molecule and the ether, and this disturbance represents a certain amount of energy and a certain total and perfectly definite transference of energy per unit of time, which definite amount of force can be used (that is, exerted on ordinary matter), but once used does not continue available.

In my opinion the idea that a definite electrical charge on a definite particle represents a definite amount of energy necessitates the above conclusion regarding the constancy of the electrical force proceeding from the charged body, similarly as regards magnetic forces. Hence it will be noticed that the gravitational force offers the only pronounced exception to a general resemblance of the forces. Perhaps it is best in this connection to call attention to the following points:

1. As regards the positive and negative tendencies of the forces, chemical, magnetic, and electrical forces show decided evidence of directive action. It is usual, moreover, to distinguish between positive and negative electricity, positive and negative poles of a magnet, and positive and negative elements, as indicating some difference in the kind of attractive force which they exert. As evidence of variation in the intensity of the molecular forces with their spatial

arrangement around the molecule, might be cited the phenomena of crystalline form, of water of crystallization and molecular combinations in general, and also those cases where a liquid appears to show a definite and symmetrical structure. The evidence that the molecular forces show positive and negative tendencies is not convincing and so a question mark is inserted in the table to indicate our lack of knowledge. With gravitational force there is no evidence showing positive and negative tendencies of the force.

2. Some might be inclined to doubt the statement that temperature has no effect upon chemical affinity. This fact is however almost beyond doubt.[1] Almost equally beyond doubt change of temperature has *per se* no effect on magnetic and electrical forces, but being unable to cite direct experiments upon this point the writer has used question marks in the table.

3. The velocity of propagation of a chemical reaction is of course an altogether different quantity from the velocity of propagation of the chemical force itself. There is no evidence as to the rate of propagation of either chemical, molecular, or magnetic forces. The velocity of propagation of gravitational force is discussed in the reference already given.[2] Electromagnetic waves travel with a velocity of 186,000 miles per second. I have taken this as indicating the speed of propagation of electrical force through the ether.

4. The law of variation of the chemical force with the distance apart of the atoms is unknown, but that this force does vary as some function of the distance apart of the atoms concerned has, I think, been already shown by the work of Richards[3] and Traube.[4] The latter says: "*Wie von mir zuerst festgestellt wurde, ist der Raum eines Atoms keine Konstante, sondern ändert sich von Stoff zu Stoff und ist um so kleiner, je grosser die Affinität des betreffenden Atomes zu den Atomen ist, mit welchen es in unmittelbarer Verbindung steht. Die Kontraktion der Atome ist daher ein unmittelbares Mass der Affinität.*" Concerning Traube's claim to priority in this discovery see remark by Richards.[5] While I prefer not to accept the conclusion of these investigators that the atoms themselves suffer a contraction, I cannot doubt from the evidence that they have brought forward that the chemical attraction between atoms is one of the deciding factors as to the distance apart of these atoms when combined into a molecule. That is to say, *the distance apart of the atoms is some function of the chemical affinity*. The problem is as yet too complicated to permit of finding the law of the attraction, and at present I must limit myself to the statement that the inverse square law of the distance is possible also with this force.

The rather widespread idea that the inverse square law is not possible for chemical force rests upon the same error already discussed for molecular force. The investigators[6] have not taken into consideration the mutual absorption or cancellation of the force by the atoms when they unite.

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[1] Trans. Am. Electrochem. Soc., 14, 35 (1908).
[2] Taylor: "Kinetic Theories of Gravitation."
[3] Proc. Am. Acad., 37, 1 (1901); 15 (1902); 38, 7 (1902); 39, 23 (1904).
[4] Zeit. anorg. Chem., 40, 380 (1904).
[5] Proc. Am. Acad., 39, 23, 583 (1904).
[6] See for instance Helmholtz: Jour. Chem. Soc., 39, 277 (1881).

In considering the numerator factor of the forces three circumstances are worthy of attention:

First. Except for the gravitational force, the numerator factor of the force is supposedly bound up with the nature of the force itself.—Thus when we speak of the "electrical" force the numerator factor has to do with the "electrical" charge; when we speak of the "magnetic" force the numerator factor is the "magnetic" strength of the pole; when we speak of "chemical" or "molecular" attraction, the numerator factor is supposedly dependent upon the "chemical" affinity or the nature of the "molecule;" when however we speak of gravitational force, it is usual to regard the numerator factor of the force as "mass," and as a property therefore distinct from and independent of gravitation. Is not "mass" really a "gravitational" charge?

Second.—Just as the condition of an electrical charge can be considered as dependent upon two factors, a capacity factor C, and an intensity factor, the voltage V, so possibly the "gravitational charge" or mass, would be dependent upon two similar factors. Similarly for the numerator factors of all of the forces.

Third.—If one attempts to consider what changes must be made in the numerator factor of the forces in order to derive a common expression for all of the forces, one starts with the broad idea that a *force is measured by the effect which it produces*. There is no law as to the conservation of force, but there is a law as to the conservation of energy. Granting the conclusion already drawn that the modified sphere of ether surrounding a particle represents a definite amount of energy belonging to the particle and that this potential energy of the particle is transformed into kinetic energy of motion by some interference of two such spheres, then it is clear that this interference of these modified spheres of ether constitutes the force of attraction acting between the particles. Now since force is transference of energy the total attractive force of a particle is definite in amount. If therefore a portion of this attraction is expended upon one particle there remains exactly

an equivalent amount less to be expended upon the remaining particles. *Consequently the attractive force exerted can be measured by the amount of the neutralized force.* From this point of view the usual ideas of the attractive forces could be expressed:

$$\text{Force} = \frac{\text{amount of attraction neutralized at unit distance} \times \text{amount of attraction neutralized at unit distance}}{s^2}$$

It seems perfectly reasonable that the attractive force should vary with the amount of the attraction absorbed at unit distance but why should the force vary as the product of the amounts so absorbed? Moreover the above expression makes the mass of a particle proportional to the amount of the attraction absorbed. Is this idea of mass further supported by the facts?

The close relationship of magnetic and electrical forces is well known. The probability of a very close relationship or, identity, of chemical and electrical forces is now hardly doubted by any one. Many chemists at heart consider molecular and chemical forces as of probably identical origin and character. Recent work shows that the motion of electrical charges *may* account for mass. Is it then too much to suspect that gravitation belongs also within the fold? And is it too much to ask that more serious attention be given to the possible ultimate identity of all of these forces?

19. *The nature of mass.*—Each of the three following definitions of mass are sometimes given:

A. Mass is quantity of matter.

B. The unit of mass is that quantity of matter which will counterpoise in a balance a certain standard mass known as a standard pound or gram.

C. Mass is inertia—resistance to motion. This is the modern definition and finds expression in the formula, energy = M. *a*. *s*. = $^1/_2$ MV^2, or mass × acceleration × distance traversed = $^1/_2$ mass × (velocity acquired)^2.

As regards definition A, compare a mass of 1 gram of lead with a mass of 1 gram of aluminum. There is not, so

far as the author knows, one iota of evidence, save in the suggestiveness of the periodic table of the chemical elements, as to whether the gram mass of aluminum and of lead contain equal or unequal amounts of the "ultimate material" of which both may be composed. And there is no way of finding out unless the aluminum and the lead can be decomposed into the ultimate constituents of which they are made. The first definition should, therefore, for the present, be banished from science.

Definition B is founded on the fact that mass is proportional to weight, or equal to $\frac{\text{weight}}{\text{acceleration}}$, and is therefore a deduction from Newton's law of gravitation.

Adopting the third definition that mass is inertia, or resistance to motion, it is certainly reasonable to consider the resistance to motion in the ether to be in principle the same as the resistance to motion in other media. If one tries to move a particle from a bar of iron, or from a piece of lead, the resistance to the motion is great. Why? Because the attraction of the particle for the surrounding particles is very great. If this attraction is overcome it becomes very easy to move the particle. If one tries to pull a boat to land, the inertia of the boat does not depend entirely upon its mass but upon the resistance the water offers to its motion.

The motion of matter through the ether must be similar. *The inertia of a body is the amount of resistance offered by the ether to the motion of the body.* The usual idea of the motion of matter through the ether has more or less neglected three facts, each of great importance.

1. *The ability of a particle to accelerate other particles towards its own position (i. e., to attract) must depend on the inertia of the particle as one factor.*—Mach declares[1] that the concept of mass as inertia renders unnecessary the special enunciation of the principle of action and reaction. Why did not Mach go one step further and apply his statement to the gravitational force?

[1] Science of Mechanics, page 220–5.

Consider a particle with the ability to attract but possessed of no inertia, and attempt to apply the principle that action and reaction must be equal and opposite. The particle without inertia and its attractive mechanism would be at once moved to the position of the attracted particle at the first effort to preserve the principle of action and reaction. A little consideration will show clearly that the *attraction*, the *inertia*, and the *principle of action and reaction*, are but phases of the same phenomenon. Their relationship will appear more clear from a concrete example. Suppose a man in a boat by means of a rope attempts to pull a man on land into the water. The man in the boat, no matter what his strength, cannot produce an effect greater than that allowed by the inertia of his boat. His greater effort would only result in drawing his own boat the faster towards land, while the man on land retains, perhaps, almost his same position, due to the fact that he can suitably brace himself so as to produce in himself a relatively great inertia. If the man on land is immovably braced to the earth the principle of action and reaction is not violated. The entire earth will be slightly moved so that the center of gravity of the entire system—earth, water, and boat—is preserved.

If both men are in boats both boats would move. The inertia of one boat, times the distance through which it moves, is equal to the inertia of the other boat times the distance through which it moves, or obviously, $Is = I's'$.

Now consider carefully the boats and the rope. If the rope is slack there is no pull (attraction) between the boats and there is no inertia actively displayed. If now the man in boat I′ pulls the rope supposed attached to boat I, he "attracts" boat I and causes at the same time a display of interia in his own boat. If the rope is attached to boat I′ and the pulling is done by the man in boat I then boat I "attracts" boat I′ and inertia is brought into play in boat I. In each case the pull upon the rope (the attraction) is possible solely because of the inertia of the boat from which the pull proceeds. *The attraction and the inertia are different ends of the*

same rope. The man in either boat might say "I can pull (attract) the other boat because of the inertia of my own boat." A man on land would say: "The rope is stressed, both boats are attracted, and both boats possess an inertia which depends on the boats themselves and on the surrounding water."

The case is exactly similar when two particles attract each other except for the fact that while the rope is the ether, the ether likewise represents the water, and is therefore one factor determining the inertia (the other factor being the nature of the particles, probably their size, if they are "ultimate" particles). Therefore, while in the case of the boats there is no necessary relation between the strength of the man in the boat and the inertia of his boat, in the case of the attracting particles, the attraction of a particle and its inertia are proportional, both being determined by the ether surrounding the particle.

Quite possibly the total attractive force of a particle depends upon the total ether surrounding the particle. Its inertia towards any given attraction depends upon the ether encountered in its motion and is therefore a function of its "front." Its acceleration is produced by the pressure of the ether from "behind." Different masses at the same distance from the attracting body have the same acceleration because the ratio of the ether pressure "behind" to the ether resistance in "front" is the same.

2. Light, heat, magnetic and electrical phenomena, also molecular and gravitational as well, show that under certain circumstances ether can react strongly with ordinary matter. Yet the ether is said to offer no resistance to the motion of a heavenly body or to the motion *per se* of other bodies. This is a remarkable, and a remarkably neglected, state of affairs.

3. The mass or inertia of a body is said to depend upon its resistance to motion in a horizontal plane and the idea and measure of mass is said to be altogether independent of the law of gravitation. This is not true as will appear upon closer inspection. The horizontal plane is defined with

reference to the center of gravity; that is, the horizontal plane is made to follow the curvature of the earth. Then motion in this plane is supposed to be free from the influence of the earth's attraction. This is unfortunately untrue, since the body will continue in motion upon the plane thus defined (even were there no air and normally no friction) only with one particular velocity. If the body is given too small a velocity it will at once press upon the plane and if it be given too great a velocity it will at once leave the plane. When the body is given such velocity that it will retain its position upon the so-called "horizontal" plane it is virtually falling around the earth.[1] Our measure of mass, therefore, so far from being free from the influence of the surrounding field of force is essentially determined by that field of force.

The idea that mass, even when it occurs in the expression $^1/_2\ Mv^2$ as one of the terms defining energy, cannot be defined or measured so as to get rid of gravitational attraction as a determinative factor will probably meet with opposition. It is well, therefore, here to recall the historical dispute over this expression between Descartes and Leibnitz and their followers—a dispute which lasted for seventy years and continues even yet to break out periodically. Descartes thought that the quantity of work in a body should be measured by the quantity of motion (MV), Leibnitz that it should be measured by the *vis viva* (MV^2). Mach in his wonderful book "The Science of Mechanics" gives a history of the dispute well worth reading and says: "Similarly, the capacity of a moving body for work, whether we measure it with respect to the time of its action by its momentum or with respect to the distance through which it acts by its *vis viva*, has no significance referred to a single body. It is invested with such, only when a second body is introduced, and in the first case, then, it is the difference of the velocities, and in the second the square of the difference that is decisive. *Velocity* is a physical *level*, like temperature, potential func-

[1] This fact hardly needs proof here. The application of the fact alone is new. For proof see almost any book on analytical or celestial mechanics.

tion, and the like."[1] (English translation, page 325.) This statement and the grounds for the statement should be carefully digested.

Some one will ask: "If the ether offers a resistance to the motion of matter why does not the earth, etc., burn up on account of the energy that would be developed through friction?" The answer is that if two bodies approach each other under the action of gravitational attraction, energy is developed and is stored up in the bodies or in the surrounding ether. It is thus that kinetic energy is made. In my opinion a body without any attractive force would not have mass in the usual sense of that term. If in motion its energy would be measured by $m'v$ and not by $^1/_2\ MV^2$ where m' is a capacity factor differing from mass as usually defined. Moreover, since gravitation acts continuously, ordinary mechanical principles holding true, we know that the action must be dynamic in its nature. There is a continual exchange of energy between the matter and the ether. Uniform motion in a circle simply means that the body is giving out exactly so much energy as it absorbs. However, I am not discussing the possible mechanism of the gravitational action in this article, except where it is essential to do so to avoid a misunderstanding of my point of view.

In conclusion, therefore, I think that mass is proportional to the resistance offered by the ether to the motion of a body and that the amount of this resistance is proportional to the amount of the attraction absorbed under a specified condition. The attraction and the mass are a sort of action and reaction due to the same cause, or rather they both depend upon the amount and the condition of the ether with which the body comes into contact. Mass is a gravitational charge. A body alone in space could not possess mass any more than a body alone in space could possess an electrical charge. Per-

[1] Mach agrees with Leibnitz and accepted scientific usage and thinks Descartes has been proved wrong. But it is worthy of note that if the ether has momentum Descartes may yet be right and his idea may be the more universal and fundamental of the two. I think this point may prove of importance in discussing the mechanism of gravitational action.

haps mass M′ in the gravitational formula, $\frac{MM'}{s^2}$, could be thought of as a positive charge (it has to do with the attraction), mass in the kinetic formula, $\frac{1}{2}Mv^2$, as a negative charge (it has to do with the inertia). They are obverse and reverse of the same thing.

Perhaps this particular idea of mass is not essential to the reconciliation of the laws of gravitational and molecular attraction, but I have felt that the succeeding statements could not be properly understood without some explanation of my point of view regarding mass.

20. *Proposed modification of the statement of the law of gravitation.*—In order to make the statement of the law of gravitation accord with the law of molecular attraction, if the views expressed in this paper are correct, two changes in our usual conception of the gravitational law are necessary:

First. The total attractive energy of a given body is to be considered a constant.—It is a property which belongs essentially to the body and to its surrounding ether. This energy is changed into kinetic energy upon the approach of other bodies and may then be given out as heat, etc.

Second. Mass in the usual sense is a relative and not an absolute property of a body.—It is proportional to the attractive forces to which the body is subjected.

The first change has to do with the *totality of the attractive force.* The second has to do with the *distribution of this perfectly definite force.*

As regards the totality of the force, if the particle or mass be supposed so surrounded with other matter that its total field of force is neutralized at distance s, then we may write as the law governing the force exerted by the particle,

27. $$\text{Force} = \frac{\mu m}{s^2},$$

where μ is, as before, an intensity factor, and where m is a factor identical with, or proportional to, ordinary mass.

This statement is intended to hold both for molecular and for gravitational force. We could conceive that the total force proceeding from a particle was absorbed by *one neighboring particle* (as was done in section 9) at the distance s, and so long as we are considering the total acting force or total obtainable energy, no error is committed But as a matter of fact we know full well that the total attractive force of one particle is not confined to a single neighboring particle. How then is this perfectly definite force distributed? Certainly to all of the particles in the immediate neighborhood, quite possibly to every particle of matter in the universe; for the statement made that equation 27 applies to the gravitational force is not to be regarded as *necessarily* a contradiction of the idea that every particle of matter in the universe attracts every other particle. It is only to be regarded as necessarily a contradiction of the idea that *every particle of matter in the universe attracts every other particle as if no other particles existed*. The difference can be made clear by analogy. The attractive force is a property of the ether and one molecule or body by affecting the condition of this ether may affect every other molecule or body. Just as a fat bather at Atlantic City may cause the water to rise in the ocean and produce an infinitesimal influence extending throughout the entire ocean even to a bather at Brighton Beach. But if some sea spirit by a process of integration, or otherwise, collects this widespread influence, he will find it definite in amount, and to consist of two factors—a capacity factor determined by the size of the aforesaid fat bather, and an intensity factor determined by his average depth of immersion. There is just so much ocean displacement and if one sea spirit makes use of a portion of that displacement he diminishes the total by an exactly equivalent amount. The mistake that has been made in the interpretation of the gravitational phenomena is not necessarily[1] in the statement that every particle attracts

[1] Perhaps the attractive influence is exerted fairly directly, perhaps by proxy. It is interesting in thinking of the possible mechanism of the force to consider how forces such as electricity, magnetism, osmotic pressure, ordinary pressure, etc., *become apparent only at a surface.*

every other particle, but in the failure to see that this statement can only be true by the *adjustment of a definite influence so as to include he universe within its scope.* If the universe were a completely static system quite possibly the attractive influence proceeding from a particle would penetrate throughout the universe and this definite amount of attraction would be felt by (would be neutralized by) every other particle in the universe in proportion to its mass and inversely as the square of its distance. Newton's law that the force between two particles = $k\frac{MM'}{s^2}$ would be exactly true. But no less true would it be that if all of the attraction proceeding from the particles were summed up, it would be definite in amount and could be expressed by $f = \frac{\mu m}{s^2}$. Under this completely static system both Newton's law, $f = k\frac{MM'}{s^2}$, and the modification proposed, $f = \frac{\mu m}{s^2}$, are equally true, one having to do with the totality of the force of the particle m, the other having to do with the distribution of this definite force.

If now the million million particles immediately surrounding m be moved closer to m, the remaining universe staying as before, the modified law proposed as governing the total force of the particle *m would remain unchanged.* Newton's law governing the distribution of the force could be applied as before after the system had become static. But it would have to be applied to *a new system.* The mass of all the particles in the universe with respect to m would have changed. It might be possible to express this change merely as a change in "k" but of this I am very doubtful. The particles immediately surrounding m would now absorb more of its attraction than they did before. *More remote particles* would absorb less. Such at least is my conception of the relation between the usual law of gravitation and the law found to hold for molecular force.

21. *Facts in accord with the suggested changes.*—1. The connection between gravitation and mass or inertia is explained as being causal, or if one objects to the word "causal," they are merely different aspects of the same phenomenon.

2. Since from the point of view outlined, mass or inertia is a necessary part of the gravitational attraction, the fact that the ether itself has no mass in the usual sense and is likewise devoid of attractive force is worthy of note.

3. It has been long known that ether under certain conditions can react with matter, as evidenced by electrical, magnetic, gravitational, molecular, and light phenomena. That ether should offer no resistance to the motion of matter is an apparent fact that needs explanation none the less because scientists try to keep quiet about it. I have here suggested that the ether does offer resistance to the motion of matter, and that this resistance has to do with the field of force surrounding the body. I have shown that the usual definition and measure of mass is not independent of, but is dependent upon, the surrounding field of force.

4. Uniform motion in a circle has always proved a stumbling block.[1] The usual explanation as to why the "falling body" does not approach the center is perhaps satisfactory, but why the accelerated body does not increase in velocity under the action of the constant acceleration (in accordance with the law, velocity = acceleration × time) is far more difficult to understand. I think perhaps a more satisfactory explanation could be given by supposing that increased velocity of the body was prevented by the resistance that the ether offered to its motion.

5. A basis is offered for explaining the fact that apparently gravitational force cannot be shielded, absorbed, or deflected, in any way. The idea is that the *mass* is a relative property and changes exactly in proportion to the change in the gravitational force. I took care to point out that in a vacuum a pound of lead, a gram of aluminum, and a feather all fell at the same rate, and that *if the mass of lead changed*

[1] "Science of Mechanism," English translation, page 160.

to the mass of the feather during their fall no observation upon the motion of the bodies could detect the change. Apply this observation *in toto* to a heavenly body. If by any means the mass of one heavenly body with reference to another was altered no observation upon the relative motion of the bodies could detect the change.

6. A basis is offered for explaining the fact that apparently gravitational force is propagated with infinite velocity, the explanation lying of course in the fact that the infinite velocity is only apparent. The alteration of mass and force takes place together and the finite velocity of propagation cannot be measured by the supposed method.

7. The gravitational force cannot be infinitely multiplied by the introduction of other particles into the field of force. The original field of force is simply readjusted, the total attractive force of each particle being perfectly definite in amount.

8. The law of gravitation comes into harmony with the law of the molecular attractive force. That the two forces are identically the same forces I have not yet proved. It may later be possible to show some relation between the constants of both forces. There are difficulties in the way of such identification. Perhaps the real solution of the identity lies yet deeper. The chemical force may be the "left over" interatomic force; the molecular force the "left over" chemical force; the gravitational the "left over" molecular force. All may be one force governed by the same law—a readjustment of a definite force taking place with each combination. The fact that the intensity of the force seems to increase enormously from gravitational to molecular, from molecular to chemical, from chemical to interatomic (as judged by radium, etc.) lends some color to this supposition. Possibly electrical and magnetic forces are different manifestations of this same fundamental force—electricity being closely connected with the chemical force and magnetism with the molecular force.

9. It is impossible here to more than mention the similarity in the behavior of the electrical force and the

gravitational-molecular. The electrical force is said to vary as $\frac{\text{charge} \times \text{charge}}{s^2}$, but in spite of this fact it is well recognized that an electrical charge on a definite particle represents a definite amount of energy and that the above law—owing to the disturbance of the field of force—is not capable of indefinite extension. I think electrical and magnetic forces could be regarded as following a law similar to the one governing the molecular force.

10. The fact that a body attracts as though its mass were collected at its center seems quite possible of explanation under the law of force given.

11. The fact that chemical changes, and physical changes of temperature and energy content, have no effect upon weight is, from the point of view given, a matter for some surprise. One explanation of this fact has been suggested by Comstock.[1]

12. The Cavendish experiment, and similar experiments, seem to indicate that consistent results under diverse conditions are obtained by writing the law of attraction, $K \frac{MM'}{s^2}$. I am not satisfied as to the explanation of these experiments. I would only point out here:

(*a*) That the experiments were nearly all performed with the idea of finding the gravitational constant, and the consequent density and weight of the earth, and usually without any intention of investigating the truth of the gravitational law.

(*b*) The essence of each experiment consists in the determination of the earth's attraction for two masses and a subsequent comparison of the attraction of the masses. *The subsequent comparison of the attraction of the masses takes place in the earth's field of force.*

(*c*) If the phenomena of electrical and magnetic attraction are considered as parallel phenomena it will be realized

[1] Jour. Am. Chem. Soc., 30, 683 (1908).

that the conclusion from these experiments, that substances attract *always* as the product of their masses, is yet open to much doubt as regards its universal application.

13. Using the usual nomenclature the electrical force can be written

$$f = K' \frac{\text{charge} \times \text{charge}}{s^2} = K' \frac{ee'}{s^2}.$$

The gravitational force can be written similarly,

$$g = K \frac{mm'}{s^2}.$$

Now if the forces are really identical we would have,

$$K' \frac{ee'}{s^2} = K \frac{mm'}{s^2} \text{ or } \frac{ee'}{mm'} = \text{constant},$$

a condition which is satisfied if e/m = constant and e'/m' = constant. From the point of view expressed in this paper the same result is reached yet more simply, the mass and the charge being measures of the same quantity in different units. It would seem therefore that the important fact that the ratio of the charge of an electron to its mass is a constant can be cited as in agreement with the views expressed in this paper.

In conclusion, I desire to say that in making the statements expressed in this paper I have not been actuated by any desire to startle or to change accepted usage. Starting originally with a research upon molecular attraction I have been led to the ideas expressed above as the best explanation of all the facts involved. Many things should be done that I have not yet been able to do. Particularly some quantitative method of testing the identity of gravitational and molecular forces should be devised. I am anxious to have my views corrected where they are wrong and to have them developed where they prove to be right. Any criticism or help publicly or privately given will be greatly appreciated by the author.

22. *Summary.*—Attention is called to a law recently discovered by the author governing molecular attraction.

The significance of this law is discussed and the law of the force deduced from it is compared with the law of the gravitational force. Careful examination of the facts would seem to indicate that perhaps the laws of gravitational and molecular force should be identical. It is shown that the gravitational law as proposed by Newton cannot apply to the molecular force and it is suggested that Newton's statement of the law of gravitation should be modified so as to become $f = \frac{\mu m}{s^2}$, when the total force of mass m is considered; that is, gravitational attraction should be regarded as a definite property of matter, and not as a property indefinitely dependent upon the *product of the masses*. The evidence for the law of gravitation as stated by Newton is discussed and the difficulties involved in the usual view of gravitation are pointed out.

Incidentally the other attractive forces, chemical, electrical, and magnetic, are discussed. The view is taken that possibly all of these forces are identical in origin and character. It is thought that the mass of a body is proportional to the attraction exerted by it and that mass is a relative and not an absolute property of matter. The bearing of the ideas suggested upon a few points is briefly discussed.

Camden, S. C.,
September 17, 1910

APATITE AND SPODIOSITE[1]

BY FRANK K. CAMERON AND W. J. McCAUGHEY

Apatite is a constituent of all rocks.[2] Consequently its presence, to some extent, should be expected in every soil, and this expectation has been confirmed by the microscopic examination of a large number of samples of various types from many parts of the United States.[3] It is slightly soluble and is hydrolyzed by water, the natural apatites yielding an alkaline solution but one also containing phosphoric acid. It has therefore an importance in soil investigations. It is a carrier of an essential plant nutrient and it is often a guide to the genesis of a particular soil. In the investigation[4] of the phosphates of lime which is in progress in this laboratory, apatite is being studied, and in this paper attention is directed to some observations which have been made upon this compound and the related substance, spodiosite.

Apatite has been reported as made artificially in several ways: by the action of phosphorus trichloride on caustic lime,[5] by passing hydrochloric acid over red hot tricalcium phosphate,[6] by melting tricalcium phosphate in sodium chloride,[7] and by melting tricalcium or trisodium phosphate in calcium fluoride or a mixture of these salts.[8] It has also

[1] Published by permission of the Secretary of Agriculture.

[2] Rosenbusch u. Wulfing: Mikrosk. Physiog. Min. u. Gest., 4 Auf. Bd. I, H. 2, 108 (1905); Emmons: Economic Geology, 3, 611 (1908).

[3] From the literature bearing on this point, the work of Retgers on the dune sands of Holland is especially interesting. See N. Jahrb. für Min., 1, 16 (1895).

[4] Bull. No. 41, Bureau of Soils, U. S. Dept. of Agriculture; Jour. Am. Chem. Soc., 26, 885 (1904); 27, 1503, 1512 (1905); 28, 1222 (1906); 32, 869 (1910); Jour. Phys. Chem., 11, 363 (1907).

[5] Debray: Comptes rendus, 32, 625 (1851); Ann. des Min., (4) 19, 684 (1851).

[6] Debray: Comptes rendus, 59, 42 (1864).

[7] Forchhammer: Liebig's Ann., 90, 77 (1854).

[8] Manross: Liebig's Ann., 82, 388 (1852); Briegleb: Ibid., 97, 95 (1856); Sainte-Claire Deville et Caron: Comptes rendus, 47, 985 (1858).

been reported as present in basic slags.[1] It has been made in the wet way.[2]

In order to obtain a pure chlorapatite of definite composition, it seemed desirable to prepare it by dissolving tricalcium phosphate in fused calcium chloride. On cooling the melt, and lixiviating with water, a granular crystalline product was obtained. A microscopic examination showed that the product was all one substance, and that it was not apatite. An analysis of the substance was made by Mr. W. H. Waggaman. This analysis, together with determinations of its crystallographic and optical properties, showed it to be a chlor analogue of the mineral spodiosite,[3] which contains relatively more halogen than does apatite.

The experiment was then tried of melting a natural chlorapatite[4] in fused calcium chloride, and lixiviating the cooled product. This procedure also yielded only chlorspodiosite[4].

Several repetitions of the experiment of melting precipitated calcium phosphate in fused chloride gave the spodiosite only, but ultimately a product was obtained which contained also some apatite. If, now, *apatite*—$Ca_3(PO_4)_2.{}^1/_3CaCl_2$—and *spodiosite*—$Ca_3(PO_4)_2.CaCl_2$—be considered as tricalcium phosphate, crystallizing with definite proportions of calcium chloride, it is apparent that the solid phase which will separate from the liquid calcium chloride at any given temperature is determined by the ratio of lime to phosphoric acid in the liquid phase, and that there is one particular ratio at which both apatite and spodiosite can exist. Consequently to ensure the formation of apatite alone, it should be sufficient to increase the ratio of phosphoric acid to lime, which obtained in the experiments just cited. This might

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[1] Stead and Risdale: Jour. Chem. Soc., 51, 601 (1887); Hutchings: Nature, 36, 460 (1887).

[2] Weinschenk: Zeit. für Kryst., 17, 489 (1890).

[3] Fiborg: G. För Förh., 1, 84 (1872); Sjögren: Ibid., 7, 666 (1884–'85); Nordenskiold: Ibid., 15, 460 (1893).

[4] An analysis of this mineral showed 5.55 percent chlorine.

have been done by passing dry hydrochloric acid through the melt, which would have been to all intents and purposes repeating the experiment of Debray cited above. Actually, it was accomplished by adding an excess of dicalcium phosphate to molten calcium chloride, cooling, and washing out the calcium chloride, when a granular crystalline product was obtained which proved to be entirely apatite. When a basic phosphate of lime was used, instead of the dicalcium phosphate, the resulting product was entirely spodiosite.

These results indicate that apatite is formed in nature under the condition that there is present some fairly strong acid in the molten magma or mother liquor. This conclusion appears to be supported by mineralogical and petrographical observations on igneous rocks where the apatite is often present as inclusions in other minerals, indicating that apatite was one of the first if not the first mineral to separate from the magma, before the excess of free acids had yet escaped.[1] The formation of both chlor- and fluor-apatite in the wet way has been accomplished in this laboratory, and will be discussed later.

Several procedures were attempted for the preparation of pure fluor-apatite. It was finally made by dissolving calcium fluoride in fused disodium phosphate, and lixiviating the cooled melt. The resulting product was a mixture of apatite and fluorite crystals. The optical properties of the fluor-apatite were determined but no chemical analysis was attempted because of the difficulty of separating the apatite from the fluorite, and no reasonable doubt can exist as to the composition of the apatite.

The artificial chlorapatite consists of long and short hexagonal prisms with bipyramidal terminations, Fig. 1. Occasionally twins are observed. The crystals vary in size from a diameter of about 0.2 mm to extremely small ones no larger than the microscopic inclusions of apatite in rocks and

[1] In connection with this, see a recent statement by Kemp: Economic Geology, 1, 230 (1906).

soil grains. The specific gravity of the pure chlorapatite is 3.010. According to Gladstone's law, this would indicate an index of refraction of 1.650. The observed index of refraction for the ordinary ray in sodium light is 1.666. This value is considerably higher than values of natural apatites as given by Rosenbusch. An examination of the analyses in Dana's system of mineralogy shows that nearly all the apatites reported are the fluor variety except those from Norway. Unfortunately the optical data of the latter have not been published. A chlor-apatite from an unknown locality has been analyzed by Mr. Waggaman, who reports 5.55 percent chlorine. The index of refraction of the ordinary ray for this chlor-apatite is 1.655. It is therefore to be expected that the

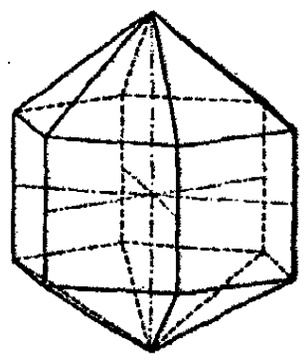

Fig. 1

pure chlor-apatite containing 6.8 percent chlorine would have a still higher index, and this is confirmed by the observations just cited. Again according to Dana the interfacial angle $0001 \wedge 10\bar{1}1$ in apatite is something over 40° but diminishes slightly as the ratio of chlorine to fluorine increases. This angle has been measured for the pure chlor-apatite just described, and the average of fairly concordant measurements on five individual crystals was found to be 39.4°. The birefringence for artificial chlor-apatite is probably less than 0.002 and that of the natural chlor-apatite is likewise low.

An analysis of the artificial chlor-apatite, by Mr. Waggaman, gave the following results:

	Chlor-apatite : $Ca_3(PO_4)_2.\frac{1}{3}CaCl_2$	
	Found	Calculated
Ca	38.0	38.5
P	18.1	17.9
Cl	6.8	6.8

The artificial fluor-apatite crystallized in elongated hexagonal prisms, terminated, however, by the basal pinacoid. This is a point of particular interest, because the artificial chlor-apatite invariably crystallized with well developed pyramidal faces, whereas the natural apatites occurring in rocks and soils, like the artificial fluor-apatite, do not show the pyramidal faces, but are terminated generally by the basal pinacoid. Moreover, the artificial fluor-apatite shows sometimes the further peculiarity of phantom crystals with a reentrant pyramid as indicated in Fig. 2. The index

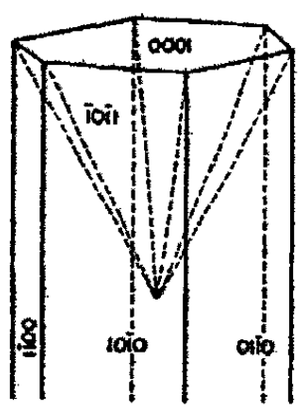

Fig. 2

of refraction of the ordinary ray for sodium light is 1.635 which agrees well with the published figures for natural apatite. The birefringence of the artificial fluor-apatite is about the same as that found in ordinary specimens of natural apatites.

Other apatites have been reported in which the chlorine or fluorine is replaced by bromine, iodine or hydroxide. Unfortunately little or nothing is known of the optical properties of these minerals, and not much more perhaps of the apatites

in which calcium is replaced by barium or other bases.[1] One compound however is of special interest here, which is apparently an apatite containing calcium silicate instead of calcium fluorite, namely, $Ca_3(PO_4)_2 \cdot {}^1/_3Ca_3SiO_5$, described by Vogt[2] as belonging to the hexagonal system. This is apparently the hexagonal mineral found in Thomas slag and described by Miers[3] who observed prisms, terminated by basal pinacoids, and sometimes showing forms, with a reentrant pyramid, like the fluor-apatites described above. Miers, however, ascribed these reentrant pyramids to cleavage. Examination in this laboratory of the yellowish hexagonal needles occurring in Thomas slag show a great similarity to naturally occurring apatites. The index of refraction for the ordinary ray is 1.630. The birefringence is weak ($\omega - \varepsilon \leqq 0.004$) and negative.

The artificial chlor-spodiosite is generally in flat rhombic tables, of the orthorhombic system as shown in Fig. 3. The

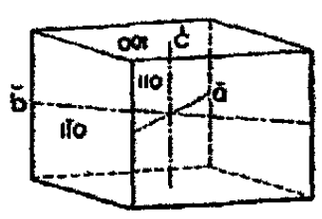

Fig. 3

crystals, 0.02–0.05 mm in diameter, consist of short unit prisms (110) terminated with a prominent basal pinacoid (001) so that they appear flattened parallel to the vertical axis. Occasionally some of the forms show a development of the brachy pinacoid (010). The mineral possesses a very good basal cleavage. The specific gravity at 23° (uncorrected) is 3.041. The prism angle $110 : 1\bar{1}0$ is 82°. The acute bisectrix (= c) is coincident with the direction of the crystal-

[1] For references to the literature, see Groth: Chemische Krystallographie, Zweiter Teil, 818 (1908).

[2] Die Silikatschmelzlösungen, 1, 5 (1903).

[3] See articles by Stead and Risdale: Jour. Chem. Soc., 51, 601 (1887).

lographic axis ($\dot{c}$). The indices of refraction determined by oil immersion methods for sodium light are

$$\begin{array}{ll} \alpha = 1.649 & \dot{c} = c \\ \beta = 1.665 \text{ where} & \\ \gamma = 1.670 & \overset{v}{a} = a \end{array}$$

The birefringence is notably high and is positive $\gamma - \alpha = 0.021$. The spodiosite found at Nordmark in Sweden occurs in orthorhombic crystals elongated in the direction of crystallographic axis $\dot{c}$, flattened parallel to a, and consequently shows prominently the brachy pinacoids (010). The unit prism (110) and pyramid (111) are next in prominence and traces of the basal pinacoid (001), macro pinacoid (100) and brachy dome (021) are found in some of the crystals. The angle $110 : 1\bar{1}0$ is given as 84°, determined with a contact goniometer.

The optical properties of natural spodiosite have not been determined but those of the corresponding magnesium analogue, *Wagnerite* ($Mg_3(PO_4)_2.MgFl_2$), are well known. The apparent difference in the angle $110 : 1\bar{1}0$ (84° in natural spodiosite and 82° in artificial chlorspodiosite) may be due to the fact that the crystals of artificial chlorspodiosite were so small that the prism angle had to be determined by rotation of the microscope stage. An error of two degrees due to slight irregularity in the faces of the minute crystals is quite possible. The error may be due to the natural shortcomings of the goniometrical method. This difference is more probably due, however, to a difference in chemical composition in that chlorine replaces fluorine, similar to the difference in angle between basal pinacoid and pyramid for chlor-apatite and fluor-apatite respectively, as pointed out by Dana,[1] and as shown by the measurements on pure chlor-apatite, the average of which is given above.

Artificial chlor-spodiosite is very slightly soluble in water, and neither it nor the artificial chlor-apatite give a solution alkaline to phenolphthalein, when boiled with water,

[1] Dana: System of Mineralogy, p. 764, 6th edition (1892).

as do all the natural apatites examined in this laboratory. The spodiosite is much more readily soluble in the presence of mineral acids than is the apatite. Heated almost to dull redness the spodiosite is completely transformed to apatite. Apparently, spodiosite is not commonly found in rocks and slags, because these latter have solidified at temperatures at which spodiosite is not stable over any appreciable range of concentration.

An analysis of the artificial chlor-spodiosite, by Mr. Waggaman, gave the following results:

	Chlor-spodiosite : $Ca_3(PO_4)_2.CaCl_2$.	
	Found	Calculated
Ca	37.8	38.0
P	14.7	14.7
Cl	16.36	16.7

To summarize the foregoing:

1. Pure chlor-apatite has been prepared. It differs from pure fluor-apatite and the natural apatites in crystal habit, and in certain optical measurements.

2. Pure fluor-apatite has been prepared. It differs from natural apatites mainly in having a tendency to form phantom crystals.

3. Pure chlor-spodiosite has been prepared. It differs from the natural fluor-spodiosite in crystal habit. Optical measurements have been made for pure chlor-spodiosite.

4. The value of certain optical measurements and interfacial angles in apatite and spodiosite respectively are determined by the ratio of chlorine to fluorine which the mineral contains.

5. Either acid conditions in the magma, or fluidity at high temperatures only, induces the formation of apatite.

6. Apparently apatite is one of the first minerals to separate from a molten magma. It is sometimes formed from aqueous solutions. It is present in all rocks and in all soils.

ON THE INTERACTION OF SODIUM AND MERCURY

BY LOUIS KAHLENBERG AND DAVID KLEIN

In 1905 Kahlenberg and Schlundt[1] found that when sodium amalgam is prepared by introducing sodium into mercury, hydrogen is evolved, which is at once oxidized and so causes the action to proceed with explosive violence. They used sodium from various sources, and the different samples all yielded about the same amount of hydrogen, namely on the average 3.24 cc for each gram of sodium employed.

The fact that metallic sodium contains hydrogen had previously been noted by Salet[2] in 1876. He claimed that the metal could be freed from its hydrogen content by heating in a vacuum. On the other hand, in 1879 Sir Norman Lockyer,[3] in the course of some investigations on the supposed complexity of the elements, found that when heated in a vacuum, sodium gave off twenty times its volume of hydrogen. Moreover, he found it impossible to free the metal entirely from hydrogen by this process.

It would naturally be assumed that the hydrogen obtained from metallic sodium, be it by amalgamation according to Kahlenberg and Schlundt or by heating the sodium according to Salet or Lockyer, is present in the metal either as occluded hydrogen or as sodium hydride. To test this further, Kahlenberg and Patten[4] prepared pure sodium hydride by carefully heating metallic sodium in a current of hydrogen, according to Moissan. It was found, however, that sodium hydride will not act on mercury, even on gently heating the two substances together. It thus appeared that the hydrogen obtained from sodium in the amalgamation process

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[1] Jour. Phys. Chem., 9, 257 (1905).

[2] Ber. chem. Ges. Berlin, 9, 354 (1876).

[3] Chem. News, 40, 101 (1879).

[4] This experiment was performed about a year after the work of Kahlenberg and Schlundt. Its result has hitherto not been published.

could hardly be ascribed to the presence of sodium hydride in the metal, and hence was probably present in the latter in the occluded form.

The object of the present investigation was to inquire somewhat further into the matter. In view of the fact that Lockyer had obtained much more hydrogen from sodium by heating the latter than was obtained by Kahlenberg and Schlundt in their experiments, it seemed specially desirable to test once more various samples of sodium as to their hydrogen content; and, if necessary, to prepare sodium that is known to be free from hydrogen (*e. g.*, by the process of heating sodium carbonate with carbon) and study its behavior on heating in a vacuum and on amalgamation. However, it was found to be quite unnecessary to prepare sodium by the special process suggested, for contrary to our expectations, the samples of metallic sodium on hand in the laboratory yielded *no* hydrogen either upon amalgamation with mercury or upon heating in a vacuum. The experiments were conducted with a relatively new sample of sodium and also with an old sample, which had been in the laboratory for several years. The latter sample was badly incrusted, but a sufficient quantity of the bright, clean metal was secured from the middle of the piece.

When the amalgamation experiment was conducted as described by Kahlenberg and Schlundt, insignificant quantities of hydrogen (amounting to less than 0.1 cc of hydrogen per gram of sodium employed) were obtained. These were no doubt due to the momentary exposure of the pieces of bright sodium to the air, which always contains moisture. That this explanation is correct appeared from the following rigorous experiment: The amalgam was prepared by using an apparatus very similar to that recently employed by Lewis and Kraus[1] in their work on the sodium electrode. Our apparatus, however, had an additional mercury manometer sealed to it. The metallic sodium was taken from the middle of a large piece which was about 4 × 4 × 20 cm. About

[1] Jour. Am. Chem. Soc., 32, 1459 (1910).

10 cc of the very clean sodium was filtered through the capillary, the pressure necessary to accomplish this being produced by means of pure nitrogen. The apparatus was evacuated as completely as possible by means of an excellent Sprengel pump. Pure, dry mercury was then distilled into the sodium. During this process, which lasted about two and one-half hours, there was a great evolution of heat, but the manometer showed no change whatever, thus demonstrating that no gas was evolved during the amalgamation process.

Another experiment was conducted to ascertain whether hydrogen is evolved when metallic sodium is heated and distilled in a vacuum. The apparatus was constructed as in the previous experiment, except that in this case the mercury manometer was replaced by a far more sensitive oil manometer, and no mercury was introduced into the apparatus at all. The sodium was from the same source as in the previous case, about 15 cc of the metal being filtered through the capillary as already described. The bulb containing the sodium was carefully heated, first in an oil bath, and then in a bath of Wood's metal, until about 8 cc of sodium had actually distilled over into the second bulb. During this process, which lasted more than two hours, the oil manometer showed a change of not more than 3 mm, which is doubtless due to the small amount of nitrogen mechanically contained in the sodium while it was being filtered.

From these experiments it is evident that even commercial samples of sodium do not always yield hydrogen either upon amalgamation with mercury or upon heating in a vacuum, and that the hydrogen obtained by Kahlenberg and Schlundt, Salet and Lockyer, in their experiments above cited was due to hydrogen occluded in the sodium which they had used.

Chemical Laboratory,
University of Wisconsin,
Madison, January, 1911

THE INFLUENCE OF ALKYL SUBSTITUENTS ON THE ELECTRICAL CONDUCTIVITY OF MALONIC ACIDS

BY WILLIAM BUELL MELDRUM

The dissociation constants of the alkyl substituted malonic acids have been determined for a few of the simpler members of the series by Ostwald,[1] Bethmann,[2] and Walden.[3] In the present communication the investigation is extended to some of the more complex acids.

The first measurements of the electrical conductivities of the malonic acids were made by Ostwald, in 1888, who determined the constants for malonic, methyl malonic, ethyl malonic and dimethyl malonic acids. He showed that like most dibasic organic acids, the malonic acids dissociate in two stages:

$$(1) \qquad (COOH).CH_2(COOH) = (COOH).CH_2(C\bar{O}O) + \overset{+}{H}$$

$$(2) \qquad (COOH).CH_2(COO) = (C\bar{O}O).CH_2(C\bar{O}O) + \overset{+}{H}.$$

He found that the dissociation of the second carboxyl group did not take place to an appreciable extent at low dilutions, and that therefore the dilution formula for binary electrolytes

$$K = \frac{m^2}{(1-m)v}$$

furnished a constant value.

Ostwald's research was followed by another by Bethmann in 1890. He made a special study of the saturated dibasic acids, and determined the conductivities of the first nine acids of the oxalic series. He showed that starting with oxalic acid the dissociation constant decreased, rapidly at first then more slowly, with the increase of the distance between the carboxyl groups. He repeated the measurements

[1] Zeit. phys. Chem., 32, 241, 309 (1900).
[2] Ibid., 5, 385 (1890).
[3] Ibid., 8, 433 (1891).

of Ostwald on the malonic acids and added two more to his list: propyl malonic and isopropyl malonic.

His determinations for the substituted derivatives of succinic acids were more extensive. For them he showed that the introduction of an alkyl group into the succinic acid molecule caused an increase in the value of the dissociation constant, the methyl and the ethyl groups having about the same effects, but two ethyl groups substituted for the two hydrogen atoms attached to one carbon atom having a greater effect than two methyl groups similarly substituted.

In a later communication, Bone and Sprankling[1] state that the dissociation constants of the normal alkyl-substituted succinic acids increase with the increase in molecular weight.

Walden, in the year following the publication of Bethmann's research, continued the work, studying the phenyl as well as a few of the alkyl derivatives. As his results are the most complete so far obtainable, a table is given below which contains for the purpose of comparison the results of Ostwald's and of Bethmann's determinations.

TABLE I

Acid	M.P.	(Walden) $K \times 10^{-5}$	(Bethmann) $K \times 10^{-5}$	(Ostwald) $K \times 10^{-5}$
Malonic	131–132° C	0.163	0.171	0.158
Methyl malonic	128° C	0.086	0.086	0.086
Ethyl malonic	110–112	0.127	—	0.127
Dimethyl malonic	185	0.076	—	0.077
Methyl ethyl malonic	119	0.161	—	—
Diethyl malonic	120–121	0.740	—	—
N-Propyl malonic	94–96	—	0.113	—
Isopropyl malonic	87–90	0.127	0.127	—
N-Butyl malonic	102	0.103	—	—
Isobutyl malonic	107	0.090	—	—

In 1892 James Walker[2] published a paper on "The Dissociation Constants of Organic Acids," which included the results for some of the alkyl-substituted malonic acids

[1] Jour. Chem. Soc., 77, 1298 (1900).
[2] Ibid., 81, 696 (1892).

together with his own results on the acid esters of the same series. The effect of substituting the ethyl radical for the hydrogen atom of one of the carboxyl groups was found to decrease the value of the constant by approximately one-half.

W. A. Smith[1] has recently further examined the manner in which dibasic organic acids dissociate. From his results he draws the important conclusion that as the dissociation constant for the dissociation,

$(COOH).CH_2(COOH) = (COOH).CH_2(C\overline{O}O.) + \overset{+}{H}$ increases,

that for the second stage,

$(COOH).CH_2(C\overline{O}O.) = (C\overline{O}O.)CH_2(C\overline{O}O.) + \overset{+}{H}$ decreases.

Wegscheider[2] has shown that the stronger the acid as shown by its affinity constant, the lower the dilution at which dibasic dissociation becomes marked.

Experimental

Carefully weighed quantities of the purified acids were dissolved in water and made up to the volume required for a 1/16 molar, or in the case of the less soluble acids, for 1/32 molar solution. The method of measuring the conductivity was similar to that described by Ostwald,[3] the resistance of the solution being determined by a standard resistance box, a Wheatstone's bridge and a telephone receiver. The temperature of the thermostat was regulated automatically by the usual electrical method, and was kept at 25° C, constant to about 0.05 of 1°. The water used was specially distilled from a solution of potassium hydroxide made with the ordinary distilled water of the laboratory, and had a specific conductivity of 2.3×10^{-6} reciprocal ohms. The corrections for the conductivity of the water were applied to the molecular conductivities and amounted to 2.35 units at a dilution of 1024 liters.

[1] Zeit. phys. Chem., 25, 193 (1898).
[2] Monatsheft, 1900, 23.
[3] Zeit. phys. Chem., 2, 561.

The bridge wire was of platinum and was carefully calibrated. The resistance capacity, or the cell constant, of the conductivity cell was found by using a 1/50 normal solution of potassium chloride which had been previously fused, the value found being 0.1007.

In the following tables the letters employed have the significations noted below.

v = dilution in cc.

M_v = the molecular conductivity at dilution v.

M_∞ = the molecular conductivity at infinite dilution.

m = the degree of dissociation.

K = the dissociation constant.

TABLE II

N-Propyl malonic acid. M_∞ (observed) = 362; M_∞ (calculated), 361. M. P. 95°–96° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	45.90	0.127	0.115
32	63.31	0.173	0.115
64	87.43	0.237	0.115
128	113.90	0.316	0.114
256	149.72	0.416	0.116
512	191.77	0.533	0.118
1024	115.64	0.627	0.122

$K = 0.115 \times 10^{-5}$

Isopropyl malonic acid. M_∞ (observed), 360; M_∞ (calculated), 359. M. P. 88°–89° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	48.60	0.137	0.135
32	67.46	0.1874	0.135
64	91.51	0.2542	0.135
128	121.07	0.3363	0.133
256	158.40	0.440	0.135
512	201.96	0.561	0.140
1024	246.24	0.684	0.146

$K = 0.135 \times 10^{-5}$

N-Butyl malonic acid. M_∞ (observed), 361; M_∞ (calculated), 360.
M. P. 98°–99° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	45.56	0.1266	0.115
32	62.93	0.1748	0.116
64	86.70	0.239	0.117
128	117.08	0.324	0.119
256	147.57	0.412	0.112
512	192.05	0.532	0.118
1024	237.25	0.657	0.122

$K = 0.116 \times 10^{-5}$

Isobutyl malonic acid. M_∞ (observed), 361; M_∞ (calculated), 362.
M. P. 104°–105° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	42.55	0.118	0.101
32	59.64	0.165	0.101
64	83.43	0.228	0.105
128	112.28	0.311	0.109
256	147.93	0.404	0.107
512	189.54	0.523	0.112
1024	233.52	0.646	0.115

$K = 0.101 \times 10^{-5}$

Isoamyl malonic acid. M_∞ (observed), 362; M_∞ (calculated), 361.
M. P. 95°–96° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	48.81	0.135	0.131
32	67.70	0.185	0.131
64	91.42	0.253	0.134
128	123.90	0.341	0.138
256	161.40	0.445	0.139
512	205.01	0.569	0.147
1024	248.15	0.687	0.147

$K = 0.131 \times 10^{-5}$

Dimethyl malonic acid. M_∞ (observed), 363; M_∞ (calculated), 362.
M. P. 190°–191° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	38.86	0.107	0.080
32	54.80	0.151	0.080
64	74.74	0.205	0.082
128	100.13	0.275	0.081
256	131.77	0.362	0.080
512	169.43	0.466	0.079
1024	208.54	0.575	0.076

$K = 0.080 \times 10^{-5}$

Diethyl malonic acid. M_∞ (observed), 361; M_∞ (calculated), 360.
M. P. 125°–126° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	105.1	0.278	0.750
32	138.1	0.382	0.750
64	179.6	0.495	0.775
128	222.3	0.614	0.784
256	264.4	0.730	0.799
512	298.0	0.827	0.752

$K = 0.750 \times 10^{-5}$

Dipropyl malonic acid. M_∞ (calculated), 361; M_∞ (observed), 360.
M. P. 157°–158° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
32	146.03	0.455	1.187
64	205.35	0.5704	1.185
128	247.70	0.688	1.186
256	288.6	0.795	1.204
512	321.86	0.893	1.455
1024	344.7	0.958	2.134

$K = 1.186 \times 10^{-5}$

Methyl N-propyl malonic acid. M_∞ (observed), 357; M_∞ (calculated), 361. M. P. 101°–102° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	60.38	0.168	0.212
32	82.06	0.227	0.213
64	109.75	0.306	0.210
128	144.91	0.200	0.209
256	184.70	0.510	0.209
512	232.17	0.641	0.224
1024	275.26	0.762	0.238

$K = 0.212 \times 10^{-5}$

Methyl isopropyl malonic acid. M_∞ (observed), 358; M_∞ (calculated), 361. M. P. 125°–126° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
32	68.81	0.190	0.140
64	93.59	0.259	0.141
128	125.20	0.346	0.143
256	162.13	0.449	0.143
512	204.91	0.568	0.145
1024	247.76	0.684	0.144

$K = 0.141 \times 10^{-5}$

Methyl N-butyl malonic acid. M_∞ (observed), 358; M_∞ (calculated), 362

$v \times 10^{-3}$	M	m	$K \times 10^5$
16	59.37	0.164	0.202
32	81.24	0.204	0.203
64	109.51	0.303	0.205
128	144.02	0.397	0.204
256	185.88	0.511	0.208
512	220.12	0.632	0.211
1024	273.61	0.752	0.221

$K = 0.203 \times 10^{-5}$

Methyl isobutyl malonic acid. M_∞ (observed), 356; M_∞ (calculated), 361. M. P. 118°–119° C

$v \times 10^{-3}$	M	m	$K \times 10^6$
32	101.71	0.282	0.346
64	130.94	0.375	0.348
128	176.83	0.489	0.355
256	220.60	0.626	0.408
512	261.31	0.737	0.407
1024	307.03	0.850	0.470

$K = 0.347 \times 10^{-6}$

Methyl isoamyl malonic acid. M_∞ (observed), 355; M_∞ (calculated), 361. M. P. 130°–131° C

$v \times 10^{-3}$	M	m	$K \times 10^6$
32	82.44	0.228	0.209
64	110.27	0.305	0.210
128	144.56	0.401	0.210
256	182.28	0.508	0.205
512	230.99	0.640	0.221
1024	272.56	0.754	0.225

$K = 0.210 \times 10^{-6}$

Ethyl N-propyl malonic acid. M_∞ (observed), 355; M_∞ (calculated), 361. M. P. 114°–115° C

$v \times 10^{-3}$	M	m	$K \times 10^6$
16	124.39	0.364	1.160
32	163.00	0.4515	1.161
64	204.72	0.567	1.160
128	249.67	0.690	1.190
256	288.64	0.800	1.241
512	321.29	0.891	1.420
1024	343.76	0.952	1.840

$K = 1.160 \times 10^{-6}$

Ethyl isopropyl malonic acid. M_∞ (observed), 358; M_∞ (calculated), 360. M. P. 72°–73° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
32	168.20	0.468	1.282
64	210.97	0.585	1.285
128	253.61	0.701	1.284
256	270.02	0.805	1.299
512	318.26	0.885	1.326
1024	340.00	0.942	1.485

$K = 1.284 \times 10^{-5}$

Ethyl N-butyl malonic acid. M_∞ (observed), 356; M_∞ (calculated), 361. M. P. 115°–116° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
32	163.11	0.452	1.161
64	205.65	0.570	1.173
128	251.66	0.686	1.165
256	294.22	0.812	1.371
512	330.64	0.916	1.939
1024	355.74	0.987	—

$K = 1.163 \times 10^{-5}$

Ethyl isobutyl malonic acid. M_∞ (observed), 354; M_∞ (calculated), 362. M. P. 102°–103° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
32	190.76	0.5284	1.852
64	234.27	0.648	1.860
128	274.59	0.758	1.860
256	291.04	0.807	1.720
512	329.55	0.910	1.790
1024	324.59	0.948	—

$K = 1.860 \times 10^{-5}$

Ethyl isoamyl malonic acid. M_∞ (observed), 355; M_∞ (calculated), 362. M. P. 115°–116° C

$v \times 10^{-3}$	M	m	$K \times 10^5$
32	156.11	0.432	1.023
64	196.58	0.545	1.020
128	237.94	0.659	1.010
256	279.35	0.771	1.019
512	310.82	0.860	1.029
1024	334.62	0.925	1.121

$K = 1.020 \times 10^{-5}$

The values of "M_∞ (observed)," as given in the above tables, were found by subtracting the ionic conductivity of sodium 49 from the molecular conductivity of the mono-sodium salt of each acid at a dilution of 1024 liters and adding on the ionic conductivity of hydrogen, 325. The values obtained for the molecular conductivities of the mono-sodium salts are as follows:

TABLE III

Acid	M at 1024 litres	Acid	M at 1024 litres
N-Propyl malonic	86.21	Methyl N-propyl malonic	81.40
Isopropyl malonic	85.60	Methyl isopropyl malonic	82.07
N-Butyl malonic	84.78	Methyl N-butyl malonic	81.69
Isobutyl malonic	85.64	Methyl isobutyl malonic	79.94
Isoamyl malonic	86.19	Methyl isoamyl malonic	79.86
Dimethyl malonic	86.81	Ethyl N-propyl malonic	79.62
Diethyl malonic	84.30	Ethyl isopropyl malonic	77.61
Dipropyl malonic	79.79	Ethyl N-butyl malonic	78.27
Ethyl isoamyl malonic	76.56	Ethyl isobutyl malonic	76.37

The malonic acids dissociate in two stages, the second carboxyl remaining intact until the degree of dissociation of the first carboxyl is about 50 percent. The second stage then begins and the conductivity increases more and more over what it would be if the acid were monobasic, as the dilution becomes greater. For this reason a satisfactory

value for the constant may be obtained only at low dilutions. Results indicate too that for dibasic acids of analogous constitution, as the value of the constant for the first stage of dissociation increases the value for the constant for the second stage decreases. From these considerations it is evident that in finding the molecular conductivity of the acid sodium salt at infinite dilution a considerable error may be introduced owing to the ionization of the remaining carboxyl, and that this error may be greater in the case of those acids which have a low value for K. Since then the values for M could not be exactly determined by extrapolation, the values at 1024 liters were taken and the molecular conductivities at infinite dilution of the acids determined from them. From these the correct values were determined.

Since at low dilutions,

$$K = \frac{m^2}{(1-m)v} = \frac{M^2}{M_\infty (M_\infty - M)v}$$

$$\frac{M_{v_1}^2}{M_\infty (M_\infty - M_{v_1})v_1} = \frac{M_{v_2}^2}{M_\infty (M_\infty - M_{v_2})v_2}$$

is an identity, if M_{v_1} and M_{v_2} are the molecular conductivities corresponding to the dilutions v_1 and v_2. Since M_{v_1}, M_{v_2}, v_1 and v_2 are known, M_∞ may be found. For calculating M_∞ by this formula, two values of M were taken which gave approximately the same values for K when the observed value for M_∞ was used. Only under such a condition would the formula give a correct result.

Discussion of the Results Obtained

In the following table the dissociation constants of the alkyl malonic acids are summarized. Those acids of similar structure are grouped together in the order of increasing molecular weights. Such an arrangement makes plain certain regularities in the variations depending on the nature of the substituting groups.

TABLE IV

Acid	Mol. wt.	$K \times 10^6$
(1)		
Malonic	104	0.158
Methyl malonic	118	0.087
Ethyl malonic	132	0.127
Propyl malonic	146	0.115
Butyl malonic	160	0.116
(2)		
Isopropyl malonic	146	0.135
Isobutyl malonic	160	0.101
Isoamyl malonic	174	0.131
(3)		
N-propyl malonic	146	0.115
Methyl N-propyl malonic	160	0.212
Ethyl N-propyl malonic	174	1.160
Propyl N-propyl malonic	188	1.186
(4)		
Isopropyl	146	0.135
Methyl isopropyl malonic	160	0.141
Ethyl isopropyl malonic	174	1.284
(5)		
N-butyl malonic	160	0.116
Methyl N-butyl malonic	174	0.203
Ethyl N-butyl malonic	188	1.163
(6)		
Isobutyl malonic	160	0.101
Methyl isobutyl malonic	174	0.353
Ethyl isobutyl malonic	188	1.860
(7)		
Isoamyl malonic	174	0.131
Methyl isoamyl malonic	188	0.210
Ethyl isoamyl malonic	202	1.020
(8)		
Malonic	104	0.158
Methyl malonic	118	0.087
Methyl methyl malonic	132	0.080
Methyl ethyl malonic	146	0.161
Methyl propyl malonic	160	0.212
Methyl butyl malonic	174	0.203
(9)		
Malonic	104	0.158
Ethyl malonic	132	0.127
Ethyl methyl malonic	146	0.161
Ethyl ethyl malonic	160	0.751
Ethyl propyl malonic	174	1.160
Ethyl butyl malonic	188	1.163

An examination of these results shows us that:

1. Any alkyl group substituted alone in the malonic acid molecule causes a decrease in the value of the constant, the decrease being greatest for the methyl group and least for the ethyl group.

2. As the number of carbon atoms in the substituting groups of normal structure increases the values of the constants converge.

3. The isoalkyl substituting groups do not show the same regularity in their relative effects, the isobutyl group especially having an abnormal effect in lowering the value of the constant when substituted alone, and in raising the value when substituted with other groups.

4. The acids containing isoalkyl groups are in general dissociated to a greater extent than the isomeric acids containing normal groups.

5. Dialkyl malonic acids are dissociated more than the isomeric mono-alkyl derivatives.

6. The introduction of one alkyl group into malonic acid is invariably attended by a lowering of the value of the ionization constant and the introduction of a second alkyl group is attended by an increase in the value of the constant over the value for malonic acid itself.

This leads to the following conclusion: the introduction of an alkyl group into the molecule of malonic acid is attended by a fall in the value of the dissociation constant; the introduction of a second alkyl group tends to lower the value of the constant still more but this tendency is more than counterbalanced by an opposing influence due to the position of the alkyl groups in the molecule. This statement holds true no matter what alkyl groups are considered though in the case of the methyl group the tendency to lower the value of the constant is not overcome by the influence due to spacial arrangement.

That in dibasic acids the proximity of the carboxyl groups affects the ionization of one of them is proved by a comparison of the constants of maleic and fumaric acids and of

ortho-phthalic and para-phthalic acids; by Bethmann's results on the dibasic saturated acids of the oxalic series, and still more conclusively by Walker's results on the malonic acid esters, which show that the replacement of the hydrogen of the second carboxyl by ethyl causes a decrease of 50 percent or more in the value of the constant.

TABLE V

Acid	$K \times 10^5$	Acid	$K \times 10^6$
Fumaric	0.093	Malonic	0.163
Maleic	1.17c	Dimethyl malonic	0.086
		Acid ester	$K \times 10^5$
P-Phthalic	0.121	Malonic	0.045
M-Phthalic	0.029	Dimethyl malonic	0.0387

This behavior Walker explains as follows: "The dibasic acids are always stronger than the monobasic acids from which they are derived by the substitution of carboxyl for hydrogen. This is owing to the effect of one carboxyl group on another. Carboxyl, in virtue of its acid character increases the dissociation of the hydrogen of a carboxyl group contained in the same molecule as itself, and this increase is the greater the more nearly the carboxyl groups occur together in the molecule."

If this be the only factor influencing the dissociation of the malonic acids then it must be assumed that the first alkyl group substituted occupies such a position that it interferes in the interaction of the two carboxyls; the second alkyl group causes a further change of the configuration of the molecule, which either causes the carboxyls to actually approach more nearly to each other or else leaves the space in the molecule between them free from interfering groups. This view seems to be supported by the fact that the influence of methyl on the conductivity of malonic acid is opposite in character to its influence on the conductivity of

succinic acid, for which difference existing theory fails to account satisfactorily.

In a future communication I intend extending the investigation to include substituted malonic acids of a more complex nature, after which we may be able to deduce more satisfactory conclusions.

In conclusion I wish to express my thanks to Dr. Walker, at whose suggestion this work was undertaken, and to Dr. McIntosh, for help and advice afforded during the investigation.

McGill University, Montreal,
February, 1911

THE TREATMENT OF SULPHATED STORAGE CELLS

BY G. A. PERLEY

If a lead accumulator is neglected sufficiently, the final outcome is the formation of white lead sulphate over the surface of the plates, while the capacity of the cell drops towards or to zero. So far as I can find, very little has been published as to the best method of treating such cells and it therefore seemed desirable to study this problem somewhat in detail.

During the discharge of an accumulator there is formed on the grids a finely-divided lead sulphate. In so far as equilibrium is reached, the sulphuric acid solution is saturated with respect to lead sulphate. The slight temperature fluctuations cause the lead sulphate to recrystallize and to form a hard crust. With rising temperature, the solubility of lead sulphate in sulphuric acid increases, and the smallest crystals dissolve. When the temperature falls a little, crystallization takes place chiefly upon the solid lead sulphate and larger flakes are formed.

A cell may become sulphated in part or wholly by an overdischarge. This may be intentional, with the object of obtaining an excessive output of electrical energy for some special reason. It may happen through local action, leakage, or internal short-circuit. There may be impurities in the lead oxides used in making the cells, deleterious substances in the lead alloys used for the grids, or there is a possibility of impurities in the electrolyte. Impurities, such as salts of iron, will undergo alternate oxidation and reduction. They will diffuse from one electrode to the other and will attack the active material. Even a small amount of an iron salt is detrimental.[1]

If too long a period elapses between discharge and charge, the conditions are exceptionally favorable for the caking of the lead sulphate. Excessive sulphating is certain to result

[1] Cf. Elbs: Zeit. Elektrochemie, 7, 261 (1900).

if the cells receive improper care when put out of commission. If the grids are only partially washed free from acid and are then allowed to dry, a uniform coating of white sulphate is sure to form.

The disastrous results of excessive sulphating are well known. Some of the most important ones are as follows: shedding of the active material, buckling, loss of capacity, increase of internal resistance, rise of temperature, etc. It is evident that the introduction of a non-conductor would tend to produce all of these results. Lead sulphate is an excellent non-conductor and hence is the cause of disaster to the cell. Since the formation of lead sulphate in the accumulator is accompanied by an increase of volume, this in itself becomes detrimental when sulphating is excessive.

Of course, the wise thing to do is to look after a storage battery so carefully that the cells never become badly sulphated. This can be done, but there are times when it is not done. People will always be careless and neglectful. When the white sulphate actually becomes visible, the feeling usually is that the cells are spoiled and that nothing much can be done with them.

A very few unsatisfactory methods of removing the sulphate have been suggested. One is to scrape off the white lead sulphate by means of a wire brush. This "carding" method removes much of the active material and therefore decreases the capacity of the cell. Such a method should be applied only as a last resort.

Prolonged charging at a low rate (one-fourth to one-half the normal charging rate) has been recommended by some. While this method gives a good reduction ultimately, the time involved is excessive and there is a very large waste of electrical energy. Charging at an abnormally high rate has also been recommended. At first it would seem as though this method and the preceding one were mutually exclusive. Some experiments soon showed that charging at a high rate is a combination of electrolytic carding with electrolytic reduction. The consumption of time and of electrical energy is

relatively low compared with the method of charging at a low rate. Against this advantage we must set the fact that the capacity of the cell is decreased owing to the removal of some of the active mass as sulphate, in consequence of the tumultuous evolution of gas.

Salomons[1] says: "Frequent and prolonged overcharging with currents about 30 percent below maximum, is the only way to reduce badly sulphated plates, which are frequently found when the cells are allowed to run too low or stand too long. When the positive plates are in a bad condition (generally due to the battery having been over-worked, *i. e.*, greatly exhausted, or owing to short circuits within the cell itself, which evidently produces a similar result, or to leakage), it is no easy matter to get them right again, since the conducting property of the paste has become very low. Under these circumstances, complex sulphates soon form and rapidly spread over the plates almost like a growth of mold. By patient and slow charging, this grey or white sulphate, from want of adherence to the healthy oxide forming below, soon falls off in the shape of scale or powder to the bottom of the pot; and care should be taken that no portion sticks between the plates.

"To return to the case for bad sulphating, a continual charging below maximum rate, half to start with, for a prolonged period will gradually reduce the unhealthy sulphate to the healthy form, and finally charge the plates by conversion of the $PbSO_4$ to PbO_2. The task is tedious, but it must not be hurried, or the positives are certain to buckle. Most of the white sulphate will fall off in scales, but should any stick between the plates, it must be pushed down with a piece of wood or a flat strip of ebonite, the latter being the best. But on no account should a piece of metal or any other conducting substance be employed for this purpose. When white sulphate exists upon the positive plates, it shows that most of the oxide has been converted into $PbSO_4$. These sulphates are very

[1] Management of Accumulators, 121, 143, 145, 147 (1906).

bad conductors. Consequently, when the white sulphate is observed, it may be concluded that a great resistance is offered to the current doing its work, and is in a manner equivalent to the plates having a much smaller active area. The maximum charging current is therefore too large; but the current may be increased as the white substance falls off or disappears. If the sulphating has become very bad, the scales often separate from the plate carrying with them blocks of paste which they overlie. This is very vexatious, for the capacity of the battery becomes much reduced by loss of active material, and great trouble is experienced in getting from between the plates these pieces, which, if not removed, short-circuit the cell.

"After bad sulphating the capacity of the cells must always be less, in consequence of the loss of some of the active material. When the fault is great, the best plan is to clean the battery.

"The cleaning of a battery consists in removing the sections from the cells (after a good charging), separating the sets of plates, and scraping the white deposit off the positives. There is no need to remove the plates from the lead strips, for, by bending them apart, plenty of room is allowed for manipulation. In cases where the plates cannot be parted, they must be reached as well as circumstances permit, and generally no difficulty occurs. The wire brush material sold under the name of 'carding' will serve to do the work. A piece of this is cut to six by four inches, and nailed to a block of wood half an inch thick, and having a handle, if found necessary, for reaching between the plates. The brush is now applied to the positives till they appear their proper color, and they are finally washed with the electrolyte and on no account with water, or sulphating will set in immediately. This done the cells are again made up, when the old solution may be used again, although it will generally be found more convenient to put in fresh electrolyte.

"If the positives are past recovery it is the cheapest to have a new set, which can be obtained from the makers at a very moderate cost in exchange for the old plates."

In Warwick's little book,[1] he discusses the effect of adding soda to the electrolyte. Some of his chemistry is queer, but the results are interesting.

"Mr. Barber-Starkey[2] found that adding a small quantity of carbonated soda to the acid electrolyte not only reduces the tendency of the elements to sulphate, but rapidly removes this salt when already formed. This action is probably due to the conversion of the sulphate, first into carbonated lead [?] and then into the peroxide, or it may be owing to the fact that sulphate of lead is sparingly soluble in a solution of sulphate of soda.

"As the results of some experiments made with a view of ascertaining the effect of adding sulphate of soda to storage battery solution, it is found that the addition of sodium sulphate to the ordinary acid electrolyte has a distinctly beneficial effect upon the working of the cell. It has been found that upon the addition of these soda salts a large proportion of the sodium sulphate is formed in close contact with the lead sulphate on the peroxide plate, and that this formation was favorable to the reduction of the latter substance, as a paste of equal parts of minium and lead sulphate is more readily reduced in solution of sodium sulphate than in dilute sulphuric acid.

"As an example of beneficial results to be derived from the use of an acid soda solution, the following may be worthy of mention. It is said that at the central News Office in Ludgate Hill, London, England, a number of large lighting cells had been idle and dry for about two years. The plates were found to be thickly incrusted with a hard white sulphate. With the ordinary electrolyte, and a charging current of from 10 to 15 amperes, no improvement was observed after two charges of eight hours per day; but after adding a half-pint of strong carbonate of soda solution to each cell, and with the same amount of current going in as before, the plates soon im-

[1] Warwick: "How to Make and Use the Storage Battery," 91, 93 (1896).
[2] Cf. Brit. Assn. Reports, 958 (1890).

proved, and in a few days all the elements presented a beautiful appearance.

"When removing sulphate by this method it is found the best way to take out the de-sulphating solution, after the plates have been brought to a healthy condition, and replace it by the ordinary dilute acid electrolyte, otherwise the negative plates are said to deteriorate."

As against this, Wade[1] found that addition of caustic soda to the acid electrolyte failed to give any very satisfactory results, the action varying without apparent reason.

In all these cases the caustic soda or the sodium carbonate was added to the acid electrolyte in relatively small amounts. Under these circumstances, the acid is nowhere near neutralized and we are dealing with a fairly strongly acid solution. When the cells are charged, there is a tendency to set free alkali at the cathode; but this is neutralized at once by the excess of acid and consequently there is a very little reduction of lead sulphate at the cathode. If the current density is very high, the amount of reduction will be increased; but it is easy to see that concordant results cannot be obtained under these conditions. The work to be described ater will show how this method can be made to give concordant results.

After we had finished the experimental work, to be described in this paper, an article on "The Rejuvenation of Sulphated Lead Storage Cells" was published by Mr. J. O. Hamilton.[2] He used a solution of caustic soda and obtained excellent results. We confirm his conclusions, but our method is more easily controlled than his.

Borntraeger[3] has suggested yet another method. Zinc plates were bound upon each side of the sulphated grids and the whole immersed in a 25 percent hydrochloric acid solution. A very satisfactory reduction is obtained in this way, but it would be very difficult to wash the chloride out completely and consequently the cell would soon go to pieces. This

[1] Secondary batteries.
[2] Railway Electrical Engineer, 2, June (1910).
[3] Zeit. Elektrochemie, 5, 325 (1897).

method suffers under the further disadvantage that it is applicable only for the negative grids. With the positive plate we should get a layer of spongy lead superposed on the peroxide. Each plate would thus be equivalent to a short-circuited cell.

The reason for taking up the study of sulphated cells was that the laboratory fell heir to twelve badly sulphated cells which were utterly useless to anybody else. The cells were made by the National Storage Battery Company. They were Type U with five plates to a cell and a rated capacity of forty ampere hours. These cells had been purchased in November, 1906, and had been used for experimental purposes until February, 1908 The cells were then put out of commission. This was evidently done too hastily. The acid was not washed out of the pores of the plates. As a result of this and of the evaporation of the water, there was an apparently uniform coating of white sulphate over each cell, when the cells were turned over to us. Since all of the cells had received practically the same usage, treatment, etc., the material was unusually satisfactory for experimental purposes.

In order to save the large cells for the final test, it seemed desirable to prepare small experimental plates. Ordinary sheet lead was cut into strips 5 cm × 10 cm. The smaller cells, made from two strips, were formed in sulphuric acid, sp. gr. 1.20, at the customary rate of 0.04 amp/cm^2 until the anode was oxidized to PbO_2. After a good coating of PbO_2 had been obtained, the cells were short-circuited and discharged to zero potential difference. This was repeated several times. Owing to the smoothness of the surface, all the lead sulphate fell to the bottom of the glass containers. Poor grids were also obtained when the charged plates were dried in the air instead of being discharged electrolytically. In order to eliminate the shedding, the lead strips were grooved by pressing a medium-meshed wire gauze against them. Little pockets were thus made and this type was placed in the usual acid and formed as before. When discharged to zero potential difference, no adherent coating of sulphate was obtained. It became evident that a porous mass is essential

to the formation of a good coating of sulphate, as this gives a larger crystallizing surface.

As a result of this experience, holes were bored at very close intervals in the 5 cm × 10 cm strips of lead. A paste of 900 grams of red lead in 150 cc of sulphuric acid (sp. gr. 1.20) was placed in these perforations and pressed until it was very compact. In this way we obtained a grid which looked much like the commercial type. After the usual charge followed by a discharge to zero potential difference, this type became sulphated. After standing a few days, the whole grid became covered with sulphate. Another method employed for making a sulphated cell, was to make a paste of chemically precipitated lead sulphate. The grooved lead plates were painted with this paste and then dried. A coherent coating was obtained in this way.

The general methods employed in the following work may be classed under three main divisions: chemical reduction; electrolytic deposition and reduction; and solvent action.

We first tried the action of ferrous hydroxide on a sulphated plate. Different mixtures of ferrous sulphate and caustic soda were tried both hot and cold; but no reduction of the sulphate could be detected and consequently this method was abandoned as useless.

We next studied Borntraeger's zinc and hydrochloric acid method. Using a 25 percent hydrochloric acid, it was found that complete reduction took place. The limitations of the method have already been pointed out. With a view to modifying the method, a more careful study of it was made. It was found that a much more dilute acid could be used, a 10 percent hydrochloric acid giving splendid results. Zinc dust was applied to the grid in the form of a paste but has a tendency to work loose and consequently does not give so good results as sheet zinc.

Hoping to eliminate the hydrochloric acid and yet to get an efficient reduction, we precipitated zinc electrolytically upon the sulphated plate, using a zinc sulphate solution containing 100 g $ZnSO_4$ per liter. A current density of one ampere

per square decimeter gave very good deposits of zinc at first. After a short time it was noticed that no more zinc was deposited. The negative grid was then removed and placed in the ordinary storage battery acid. A fine partial reduction took place. Even when working with a concentrated solution of zinc sulphate not enough zinc could be precipitated to cause complete reduction of the lead sulphate. The cause of the trouble seems to be the sulphuric acid set free at the anode. Various methods were tried in order to eliminate this trouble. Zinc oxide and carbonate were both added in excess to the solution of zinc sulphate but without avail. Being insoluble, they settled to the bottom and the circulation is not sufficiently rapid to keep the solution between the plates in an approximately neutral solution. Since the positive and negative grids are very close together, the diffusion of the acid takes place very readily. With an excess of acid, hydrogen is set free instead of zinc.

When the current density was increased to three amperes per square decimeter, a deposit of zinc could be obtained on the sulphated grid in spite of the excess of acid; but a new difficulty arose. With the increased drop of potential through the solution, there came an increased tendency of the zinc to deposit on the best-conducting portion of the grids and to form trees. When this happened, the sulphate was torn off the grid and the active material was consequently wasted.

Under the best conditions this method only cures the sulphating of the spongy lead plate partially. At the anode there was a partial oxidation of the lead sulphate to lead peroxide owing to the low acid content of the initial zinc sulphate solution. When this method was tried on one of the large cells, the cell was brought back from practically zero capacity to about 75 percent of its rated capacity. While this is not a bad result, the method is expensive and inconvenient. Since we have worked out a much better method, we do not recommend this one.

A method very similar to the preceding one was also tried. Aluminum and caustic soda were substituted for zinc

and hydrochloric acid. This combination also reduces lead sulphate. When an aluminum sulphate solution was electrolyzed, practically the only action on the grids was a "carding" one, so no further tests along this line were made.

Under the second heading—that of electrolytic deposition of lead and subsequent electrolytic reduction of the sulphate in acid solution—there seemed to be great possibilities. If lead could be deposited in suitable form all round the particles of lead sulphate, it would then be a very simple matter to reduce the lead sulphate electrolytically. To test this, lead was deposited under varying conditions from plumbite, fluosilicate, acetate, and perchlorate solutions. The deposition was always accompanied by great shedding of the lead sulphate, due to the treeing of the deposited lead. This method was therefore ruled out as unsatisfactory.

With the third type—that of solvent action followed by re-deposition of the lead—we tried such solvents for lead sulphate as sodium acetate and sodium tartrate. Some of the lead sulphate was removed; but the re-deposition of the active material, thus removed, was far from satisfactory. Consequently no capacity tests on the large storage cells were made by this method.

During some experiments with ferrous hydroxide, in which an excess of sodium hydroxide was used, it was noticed that where the sodium hydroxide came in simultaneous contact with lead and lead sulphate, very beautiful crystals of lead were deposited. It seemed that a somewhat closer study of this phenomenon would be desirable. One of our sulphated lead grids was immersed in a solution containing 500 g NaOH per liter. The sulphate disappeared completely and splendid crystals of metallic lead were found deposited on the lead strip. On repeating the experiment, it was noticed that there was an intermediate formation of a greenish yellow salt. The most plausible explanation of this unexpected phenomenon was that it was due to impurities in the lead or in the solution which caused a reduction. To test this, a solution of sodium hydroxide was prepared from C. P. sodium peroxide and distilled

water. The lead sulphate was prepared from C. P. chemicals and the lead was tested carefully. In spite of all these precautions, the lead sulphate disappeared and crystals of lead were formed. The results of one series of experiments is given in Table I.

TABLE I

No.	g Na_2O_2	Equivalent to g NaOH per liter	Time	Results	
				First	Final
1	8.4	65	46 hrs.	yellow	lead
2	9.48	70	46 hrs.	yellow	lead
3	10.15	75	46 hrs.	yellow	lead
4	10.8	80	46 hrs.	yellow	lead

Similar results were obtained when pure, electrolytic lead was covered with sulphate.

Having thus eliminated the possibility of any reducing agent in the solution or the lead, it was next thought that in some way a concentration cell had been formed and that the crystals of lead were due to the action of the hypothetical concentration cell. To test this assumption, a cylindrical, rotating, lead grid was covered with sulphate and placed in a caustic soda solution, No. 4 of Table I. After only twenty-seven minutes' rotation some reduction of the lead sulphate had taken place.

Since guessing seemed to be unprofitable, we then decided to ascertain the most effective concentration of sodium hydroxide. The results are given in Table II.

TABLE II

No.	g Na_2O_2 in 300 cc H_2O	Equivalent to g NaOH per liter	Surface in cm^2	Results
1	23.40	80	40	Excess yellow salt, deposit too loose
2	21.94	75	40	Excess yellow salt, deposit too loose
3	20.48	70	40	Too loose a deposit
4	19.01	65	40	Fine reduction in three hours
5	14.63	50	40	Reduction but in too long a time

Thus we see that a concentration of 65 g NaOH per liter is the best. In Table III are some data which show that the presence of metallic lead is essential.

TABLE III

No.	Reaction	Results
1	NaOH on $PbSO_4$	No effect
2	Sodium plumbite on $PbSO_4$	No effect
3	NaOH on $PbSO_4$ in presence of lead	Complete reduction

The experiments described show that the apparent reduction of lead sulphate by sodium hydroxide is not due to impurities in the lead, the lead sulphate, or the caustic soda; and that the reaction does not occur when metallic lead is absent. Just how the lead acts is not yet clear.

In all the experiments in which crystals of lead were obtained, there was always the intermediate formation of a yellowish green substance. As yet, we have not obtained this substance in a pure enough state to warrant an analysis. A mixture of metallic lead with some of the yellowish green material was treated with different reagents. The results are given in Table IV.

TABLE IV

No.	Reagent	Result
1	H_2SO_4	No effect
2	NH_4Cl	Insoluble
3	H_2O_2 (in KOH)	No effect
4	$Pb(CH_3CO_2)_2$	Insoluble
5	HCl	Slightly soluble
6	HNO_3	Turns white
7	CH_3CO_2H	Completely soluble

Attempts were made to separate the lead from the yellowish green salt by floating the latter out. Chloroform was tried as the medium but tended to decompose the salt, and no clean separation was obtained. From Table IV we see that the intermediate salt (in presence of lead) does not behave

like any of the oxides of lead or like plumbic sulphate. The time at our disposal did not permit any further study of this interesting reaction, but the matter will be taken up later in this laboratory.

Since sodium hydroxide has such an effect on lead sulphate when the latter is in contact with metallic lead, attempts were accordingly made to apply this economically in the case of the sulphated storage cell. If a sodium sulphate solution is electrolyzed between two sulphated lead grids, the action of the current would tend to form caustic soda at the cathode. The cathode would then react with the caustic soda just as in the experiments previously described. In fact, the reduction of the lead sulphate should be extremely efficient, because the caustic soda would be formed just where it was needed, in the pores of the grid.

At the anode we should expect to get a more efficient oxidation of the lead sulphate to lead peroxide with a sodium sulphate solution than with a sulphuric acid solution. The potential of oxidizing agents is higher in a strongly acid solution than in a neutral or alkaline one and consequently it is easier to oxidize a substance to a higher stage of oxidation, other things being equal, in an alkaline or slightly acid solution than in a strongly acid one. It ought therefore to be possible to regenerate both plates of the battery simultaneously.

Varying concentrations of sodium sulphate were tried and it was found that the best results were obtained with a concentration of 45 grams per liter. The data are given in Table V.

TABLE V

Electrode surface = 40 cm^2; current = 0.5 amp.; time = 8.5 hr.

g Na_2SO_4 per liter	Results		g Na_2SO_4 per liter	Results	
	Anode	Cathode		Anode	Cathode
30	shedding	poor	45	good	good
35	shedding	poor	50	shedding	shedding
40	less shedding	fair	80	shedding	shedding

Before applying these results in the final tests, some experiments were made with caustic soda and sodium carbonate solutions. The electrolysis of a sodium hydroxide solution should give us the maximum reduction at the cathode and maximum oxidation at the anode. The difficulty is that it is too efficient. Varying concentrations of sodium hydroxide were tried but the reduction is usually so rapid that grids were formed which began to shed after a little service. The manipulation or control of this solution is not easy unless one has had a great deal of practice. While a sodium hydroxide solution can be made to give good results, it is not so satisfactory as a sodium sulphate solution. Varying concentrations of sodium carbonate were also tested. The results are similar to those with the caustic solutions and for the same reasons.

The experiments with the home-made grids indicated that a concentration of about 45 g anhydrous sodium sulphate per liter should be the best; but the difference between our temporary grids and the commercial ones was so great that we did not feel at all certain that it was safe to reason from one to the other. Some actual runs were therefore made at various concentrations.

In order to obtain a comparison, one cell was charged and discharged a great many times at the normal rate with sulphuric acid as electrolyte. The data are given in Table VI.

TABLE VI

Five plates, normal capacity 40 ampere hours

Total input	903 amp. hours
Total output	519 amp. hours
Initial capacity	1 amp. minute
Normal capacity	40 amp. hours
Final capacity	27 amp. hours
Percentage capacity	67.5 percent

While it might be considered rather a feat to bring the cell from zero capacity nearly to 70 percent of its initial capacity, the run was not really satisfactory. The cell was in very poor

shape after this treatment, as the active material began to disintegrate and to shed.

Another cell of the same type was filled with sodium sulphate solution and charged at the normal rate until the reduction was complete. This took about 60 hours. Two lead dummies were placed in the container so that the end plates should be reduced rapidly. The data are given in Table VII.

TABLE VII

Five plates, normal capacity 40 ampere hours.

Anhydrous sodium sulphate	140 grams per liter
Initial capacity	1 amp. minute
Normal capacity	40 amp. hours
Final capacity	36 amp. hours
Percentage capacity	90 percent

A similar run was made with sodium carbonate as electrolyte instead of sodium sulphate. The reduction was about one-third the number of ampere hours required with the sodium sulphate solution but this apparent advantage is much more than counterbalanced by the deposit being too dense and by the excessive shedding. Only about 53 percent of the normal capacity could be obtained.

To test the effect of concentration of sodium sulphate, runs were made with a saturated solution and with a solution containing about 91 g hydrated sodium sulphate (equivalent to 40 g anhydrous salt) per liter. The data are given in Table VIII.

TABLE VIII

Five plates, normal capacity, 40 ampere hours

Sodium sulphate	Saturated solution
Initial capacity	1 ampere minute
Normal capacity	40 ampere hours
Final capacity	46 ampere hours
Percentage capacity	115 percent
Anhydrous sodium sulphate	40 grams per liter
Initial capacity	1 ampere minute
Normal capacity	40 ampere hours
Final capacity	50 ampere hours
Percentage capacity	125 percent

These cells have been giving these high percentage capacities right along since then, so there is no chance for error in regard to the facts It is of course impossible to say whether these two cells were originally better than the other two cells of the same lot or whether there was some difference in the amount that they were used before they were allowed to spoil. All the plates in all the cells were covered with an apparently uniform shell of white sulphate, and the important thing is that they can be brought back into such good condition. It would not be safe to conclude from the two experiments tabulated in Table VIII that the dilute sodium sulphate worked any better than the concentrated solution. About 30 percent more ampere hours were necessary to produce complete reduction in the dilute solution than in the concentrated one and this difference is unquestionably a real one. So far as one can judge, the concentration of the solution is important only to the extent that the reduction takes place more rapidly in the concentrated solution than in the dilute one.

The tests so far had all been on cells which had become sulphated under rather unusual conditions. We have therefore tested two other wrecks on which we were able to lay our hands. The first was an old and badly buckled cell which was rescued literally from the scrap heap The data are given in Table IX.

TABLE IX

Nine plates, normal capacity 60 ampere hours

Anhydrous sodium sulphate	120 grams per liter
Initial capacity	26 ampere hours
Normal capacity	60 ampere hours
Final capacity	48 ampere hours
Percentage capacity	80 percent

This condemned cell was restored so as to give 80 percent of its original capacity. Considering the condition it was in, this was as much as anybody could hope for.

Another cell was only partially sulphated over the surface but had been allowed to stand discharged for a long time. The data are given in Table X.

TABLE X

Two plates, normal capacity, 12 ampere hours

Anhydrous sodium sulphate	152 grams per liter
Initial capacity	3.75 ampere hours
Normal capacity	12 ampere hours
Final capacity	11.75 ampere hours
Percentage capacity	98 percent

Although this cell was apparently in poor shape, it was restored practically to its original state. These illustrations suffice to show the general applicability of the method.

When one starts with a battery in commission, the acid should be siphoned off and the solution of sodium sulphate run in. It is desirable, but not necessary, to place dummy plates outside the end plates. The cell can then be charged at the normal rate until the sulphate is entirely reduced. This can be determined by the eye; but, if that is inconvenient, a charge of sixty hours will probably be satisfactory. The sodium sulphate should then be siphoned off and the grids washed once with water. The amount of sodium sulphate remaining in the plates will have a beneficial rather than a deleterious effect. If the water is then drawn off and the normal battery acid run in, the battery should be as good as new, always supposing that the only damage is due to sulphating. In our tests the current efficiency was only about 80 percent, which is probably lower than it was when the cell was new, though we have no data on that point.

The cost of restoring a cell is low. For the small 40 ampere hour cells which we have studied, it has taken less than a kilowatt hour to bring them back to good condition. That means not over ten cents per cell for electrical energy. Sodium sulphate is cheap and can of course be used over and over again. While good results can be obtained with almost any concentration of sodium sulphate, the time necessary for reduction is increased when the solution is relatively dilute. On the other hand a saturated solution is objectionable owing to the possible crystallization. An arbitrary concentration of 200 grams $Na_2SO_4.10\ H_2O$ per liter is therefore recommended.

The process as outlined is very efficient and has the further advantage that it introduces no deleterious substances into the cell. Of course it is absolutely essential that the sodium sulphate shall be pure. The ordinary sodium sulphate always contains chloride. With chlorine in the cell the destruction of the plates is only a matter of time and not of very long time at that.

A representative of one of the large storage battery companies has stated that any sulphated cell which he has ever tested could be restored by charging for a long enough time at about half rate in the regular battery acid. No data have been published and consequently one does not know what the maximum degree of sulphating was or what the length of time was. Where the time involved is not excessive, this method has the advantage of eliminating the transfer of electrolyte.

If the time involved is excessive, as it is likely to be in the case of badly sulphated cells, the cost of time and of electrical energy will exceed the cost of handling. It would be a mistake to make any hard and fast rule as to which method to employ; but it seems probable that a prolonged over-charge at half rate in the regular battery acid will suffice for cells which are not badly sulphated. For extreme cases of sulphating the sodium sulphate method is unquestionably the only one which can be used. A special series of tests would be necessary to determine the relative merits of the two methods for intermediate cases.

The general results of this paper are as follows:

(1) A badly sulphated cell can be restored by charging at the normal rate in a sodium sulphate solution.

(2) It is desirable, but not necessary, to use lead dummies outside the end plates.

(3) A concentration of about 200 g $Na_2SO_4.10H_2O$ per liter is recommended but the concentration can be varied within very wide limits.

(4) It is essential to the life of the cell that the sodium

sulphate should meet the requirements as to purity which are laid down for battery acid.

(5) A very badly sulphated cell can be restored by about sixty hours' charge at normal rate.

(6) The cost of electrical energy to restore a 40 ampere hour cell should not exceed ten cents.

(7) Since sodium sulphate is not deleterious to the cell, it is not necessary that the sulphate solution should be washed completely out of the pores of the plates.

(8) It has been stated by others that a cell can be restored by charging a half of the normal rate for a long time in the regular battery acid. It seems probable that the time and electrical energy required would be excessive in the case of very badly sulphated cells.

Most of the experimental work recorded in this paper was done by Messrs. Daley, Graham, and Martin as senior research work. I am indebted to Mr. C. W. Bennett for some runs made after I left. The work was suggested by Professor Bancroft.

Cornell University

NEW BOOKS

Electrical Nature of Matter and Radioactivity. *By Harry C. Jones. 15 × 22 cm; pp. ix + 210 + xv. New York: D. Van Nostrand Company, 1910. Price: $2.00 net.*—The headings of the chapter are: the electrical conductivity of gases; the determination of the mass of the negative ion in gases; nature of the corpuscle and the electrical theory of matter; the nature of the atom in terms of the election theory; the X-rays; the discovery of radium; other radioactive substances in pitchblende; the alpha rays; the beta and gamma rays; other properties of the radiations; production of heat by radium salts; emanation from radioactive substances; helium produced from emanation; induced radioactivity; production of radioactive matter; theoretical considerations; wide distribution of radioactive matter and the origin of radium.

"The aim of the writer has been to present the more important facts and conclusions in connection with the work on the 'Electrical Nature of Matter and Radioactivity' as far as possible in non-mathematical language. This has been done with the belief that there are a large number of those who have a truly scientific interest in these most recent and important developments in physics and physical chemistry, but to whom a more technical and rigidly mathematical treatment might not appeal."

There is a curious omission of the units on p. 3. "The ratio of the charge carried by these ions [of an electrolyte] to their mass has been determined. In the case of hydrogen ion, which is the characteristic ion of all acids, it has been found to be of the order of magnitude of 10^4.

"It was recognized to be of importance to determine the ratio of the charge to the mass of the ion in gases. If we represent the charge carried by the gaseous ion to be e, and the mass of the ion by m, the ratio in question is e/m."

Wilder D. Bancroft

A Text-Book of Organic Chemistry. *By A. F. Holleman. Edited by A. Jamieson Walker, assisted by Owen E. Mott, with the co-operation of the author. Third English edition, partly rewritten. 15 × 23 cm; pp. xx + 599. New York: John Wiley & Sons. London: Chapman & Hall, 1910. Price: $2.50.*

The second English edition was reviewed three years ago (12, 717). In this third English edition the most important change is that the chapter "treating of the proteins has been rewritten, and is now placed after the sugars along with the chapter on amino-acids, so that it is no longer an appendix to the system of classification of organic compounds but is incorporated with it."

The author has given the trade names of rodinal and amidol under the appropriate chemical compounds. It would not be a bad plan to extend this practice so as to include some of the other photographic developers such as metol, edinol, and adurol. Since $Na_2S_2O_3$ is so widely known as sodium hyposulphite, it seems an error of judgment to call $H_2S_2O_4$ hyposulphurous acid, p. 561, even though there is excellent authority for so doing. *W. D. Bancroft*

POTASSIUM AMMONOPLUMBITE

BY EDWARD C. FRANKLIN

SOCIÉTÉ CHIMIQUE DE FRANCE BIBLIOTHÈQUE

Some years ago while engaged in studying the action of potassium amide on liquid ammonia solutions of lead salts,[1] the writer noted the probable formation of a compound related to ammonia as the salt, potassium plumbite, is related to water; and at the same time he promised to pursue the subject further and, if possible, to determine definitely the composition of the compound formed.

When a lead salt, for example lead nitrate, is treated in aqueous solution with a solution of potassium hydroxide, the precipitate of lead hydroxide first formed dissolves in an excess of the alkali with the formation of a salt, usually called potassium plumbite, the composition of which is not certainly known.[2] The action may be expressed by the equations,

$$Pb(NO_3)_2 + 2KOH = Pb(OH)_2 + 2KNO_3,$$
$$Pb(OH_2) + KOH = KOPbOK + H_2O.$$

In a similar manner, as was pointed out in the paper cited above, a lead salt in liquid ammonia solution reacts with a solution of potassium amide to give a precipitate of lead imide in accordance with the equation,

$$PbI_2 + 2KNH_2 = PbNH + 2KI + NH_3,$$

and this precipitate was found to dissolve readily in an excess of potassium amide with the probable formation of the analogous ammono salt, PbNK.

The experiments described in this paper show that a

[1] Jour. Am. Chem. Soc., 27, 843 (1905): Zeit. anorg. Chem., 46, 1 (1905).

[2] Woods: Jour. Chem. Soc., 97, 878 (1910). Hantzsch (Zeit. anorg. Chem., 30, 289) suggests that the compound formed by the action of potassium hydroxide on lead hydroxide may be the lead analogue of potassium formate. He accordingly names the substance potassium plumboformate and gives it the formula HPbOOK. In a similar manner the compounds described in this paper may be formulated as derivatives of tetravalent lead as follows: $HPb(NH)NHK$, $HPb(NH_2)_2NHK$, and $HPb(NH_2)_3NHK.NH_3$.

compound of the nature surmised is in fact formed in accordance with the equation,

$$PbNH + KNH_2 = PbNK + NH_3,$$

when lead imide, an amphoteric imide, is dissolved in an ammoniacal solution of potassium amide.

The substance thus formed takes a place in the ammonia system of acids, bases and salts analogous to that occupied by potassium plumbite in the ordinary water or oxygen system, and is therefore properly named potassium ammonoplumbite.

Preparation of the Salt.—Pure, dry lead iodide, together with a small quantity of platinum black, are introduced respectively into the two legs of the reaction tube after the manner described in former papers.[1] After the conversion of the metallic potassium into potassium amide, the solution of lead iodide is run rapidly into the solution of potassium amide until a permanent precipitate of lead imide begins to form. Thereafter the lead iodide solution is added more carefully so long as the formation of lead imide continues. Care must be exercised to avoid any excess of the lead iodide solution, and to keep the precipitate thoroughly agitated, as otherwise the lead imide will be contaminated with ammonobasic salt.[2] The lead imide thus formed is washed free of the other product of the reaction, namely, potassium iodide, after the manner previously described.[3] The leg containing the pure lead imide together with sufficient ammonia to well cover the precipitate is then immersed in a bath of liquid ammonia contained in a Dewar vessel, the ingress to the preparation tube is connected by means of small lead tubing[3] with a stock cylinder of liquid ammonia, the plug of the glass stopcock is removed and a slow current of ammonia gas is turned on. This ammonia stream is for

[1] Jour. Am. Chem. Soc., 27, 830 (1905): Fitzgerald: Ibid., 29, 660, 1694 (1907).

[2] Cf. Jour. Am. Chem. Soc., 27, 845 (1905).

[3] Loc. cit.

the purpose of preventing access of air and moisture during the succeeding operations. The arm of the reaction tube containing the potassium iodide and unused lead iodide is then opened and its contents removed by solution in liquid ammonia contained in a Dewar cylinder. A fresh supply of metallic potassium is then introduced and the tube is again sealed before the blow pipe. After the metal is converted into the amide the solution of potassium amide is carefully poured upon the lead imide until the latter is dissolved. The one leg of the apparatus now contains a solution of potassium ammonoplumbite mixed with more or less potassium amide and with any potassium iodide resulting from basic salt with which the lead imide may have been contaminated, or which may not have been removed from the precipitate by the washing described above. The other leg contains unused potassium amide solution.

The subsequent operations of purifying the salt for analysis will be more easily followed by reference to the Figs. 1 and 2. In order to remove the unused potassium amide solution and at the same time to get the apparatus into a more convenient form for the final purification of the salt, the leg *B*, Fig. 1, is sealed off at *B*, thus removing the unused potassium amide solution and at the same time changing the apparatus into the form shown in Fig. 2. While these operations are in progress the two legs of the apparatus are kept cold, each in a bath of liquid ammonia, and the stopcock is opened into a three-way tube carrying a current of ammonia gas as indicated in the figure. The stopcock must be open in order to equalize the pressure inside and outside the tube during the operation of sealing off leg *B*, while the current of ammonia gas prevents access of air to the apparatus and also serves as a source of the slight pressure necessary in shaping the lower end of the tube *B* before the blowpipe. Momentary closing the exit of the three-way tube brings the necessary pressure for the purpose into existence. The stopcock is then closed and the apparatus is removed from the bath of ammonia and allowed to stand at laboratory temperature until

the platinum black and other solid impurities have subsided, after which the clear solution of the salt is decanted into leg *B*. Leg *A* is then maintained at a slightly lower temperature than leg *B* and ammonia is allowed to distil from *B* into *A* until a satisfactory crop of crystals of the salt has separated, after which the mother liquor is drained from the crystals into leg *A*. The drainage of the mother liquor is

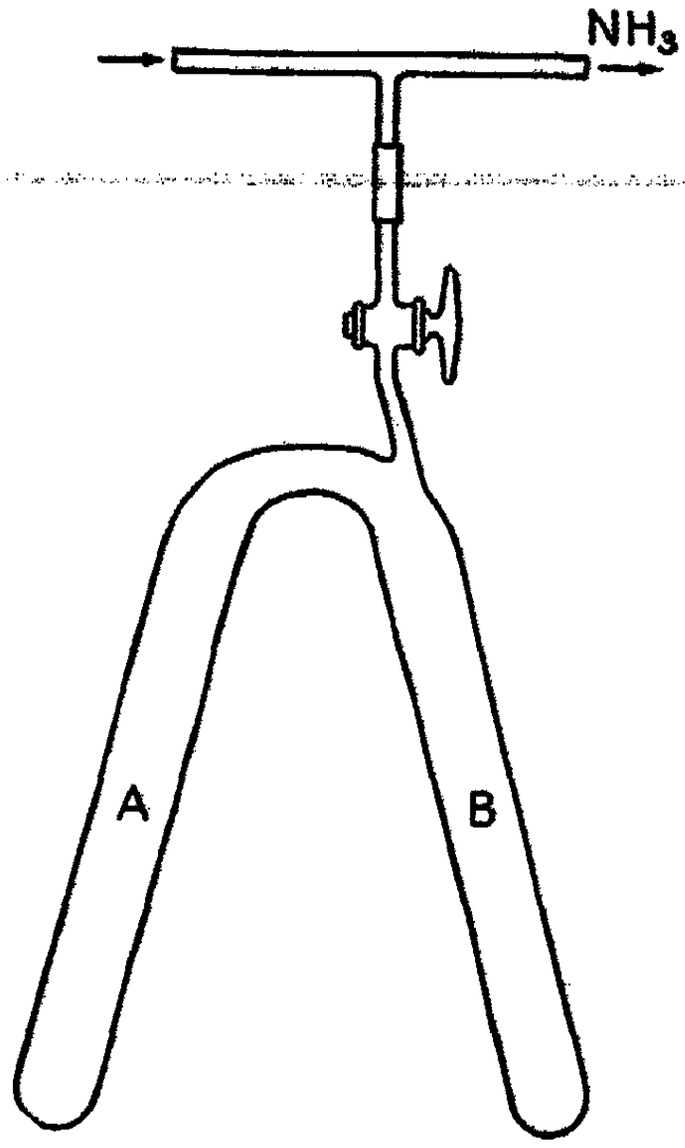


Fig. 1

facilitated by judicious applications of a swab of cotton, moistened with liquid ammonia, to the exterior of the tube. Sufficient ammonia is then distilled back into *B* to dissolve the crop of crystals. The solution thus formed is again evaporated and the operation of recrystallizing the salt is repeated as many times as may be considered necessary. The legs

A and *B*, containing respectively the mother liquors and the solution of the pure potassium ammonoplumbite are now immersed in liquid ammonia and sealed apart at *C*, ingress of air being prevented by the use of the device described above. A solution of the pure salt contained in a receptacle suitable for weighing is thus obtained.

Determination of the Ammonia of Crystallization.—The

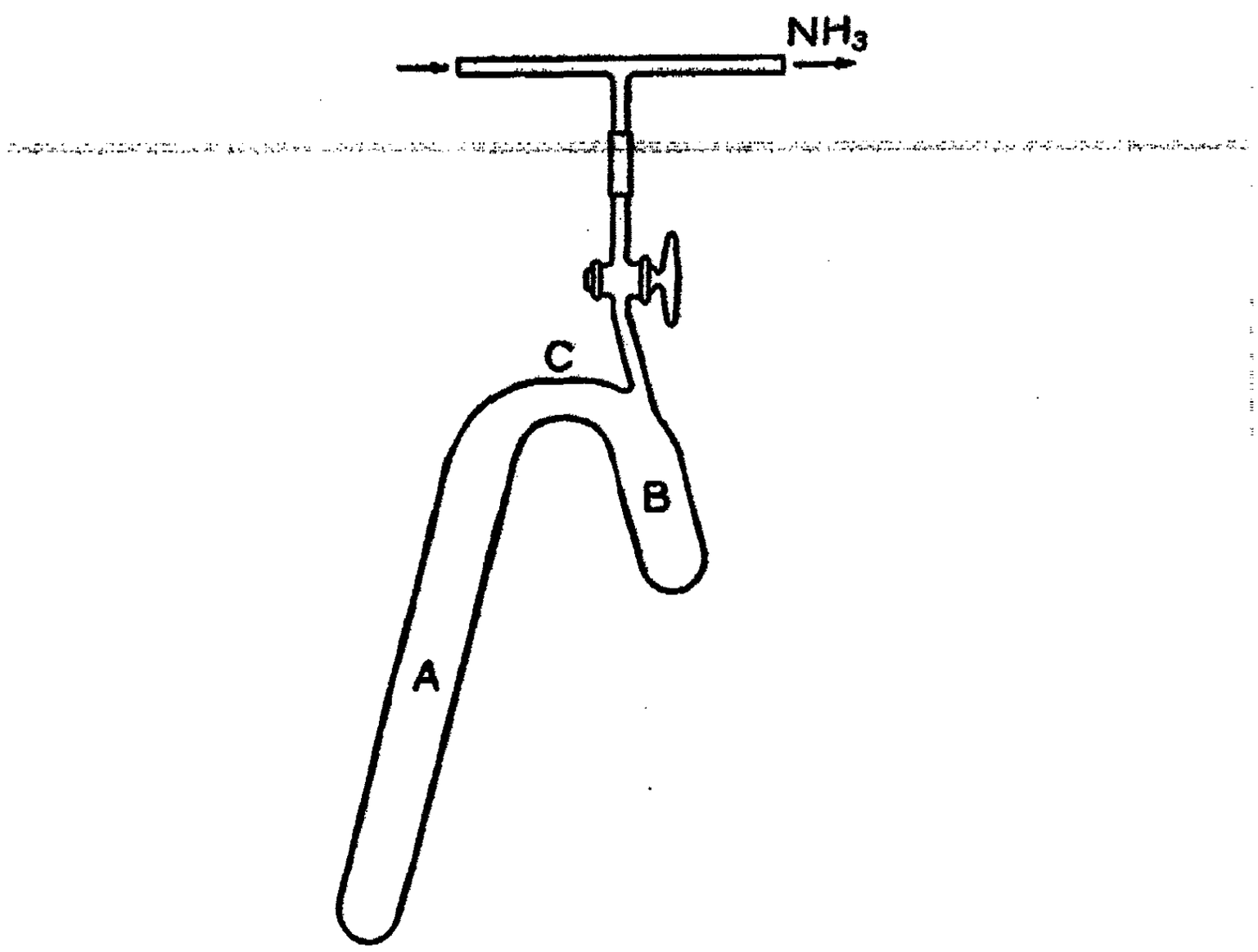


Fig. 2

earlier specimens were prepared for analysis by simply allowing the solvent to evaporate and removing the residual gas from the tube by means of an air pump at laboratory temperature. The results of the analysis of one of these preparations, obtained after the sacrifice of a number of experiments to the development of a method of experimental

procedure and to the acquisition of the necessary manipulative skill, show its composition to have been $PbNK.2NH_3$. From the effloresced appearance of the dried salt it was obvious that a portion of the ammonia with which the salt had crystallized from solution had been given off. Later preparations were therefore submitted to the following described treatment with the object in view of determining the amount of ammonia of crystallization present in the uneffloresced salt and also the total amount of ammonia removable at temperatures up to such as might lead to the explosion of the compound.

The preparation tube containing the salt, together with an excess of solvent, and immersed in a bath of liquid ammonia, *A* Fig. 3, is connected with a Sprengel pump provided with a vacuum gage, *B*. As ammonia is removed through the pump the gage shows a constant tension of the ammonia gas so long as any excess of saturated solution remains mixed with the crystals of salt in the preparation tube. A sharp fall in the pressure indicates the point at which all excess of solvent has disappeared. The salt is thus dried at a temperature some ten or more degrees below the boiling point of the solvent, temperatures which the liquid ammonia assumes automatically when the bath is open freely to the atmosphere. The gas still remaining in the preparation tube is then removed by means of the pump, or the amount is calculated from the observed pressure and temperature and the known volume of the tube. The preparation tube, containing the uneffloresced salt, is then disconnected from the pump and weighed. Reattached to the pump, the removal of ammonia is continued at 20° until the pressure of the gas shows a sharp decline to zero. The tube is then detached from the pump and weighed again. Again connected to the pump, the tube and its contents are heated *in vacuo* to 80°–100°, in some cases to 130°–140°, so long as the salt continues to lose ammonia.

Failing to obtain entirely satisfactory results on the specimens treated in accordance with the above described

procedure, the apparatus was so altered, *C*, *D*, Fig. 3, as to enable the operator to distil liquid ammonia into the preparation tube, thus permitting a repetition of the determination of the ammonia of crystallization on one and the same specimen.

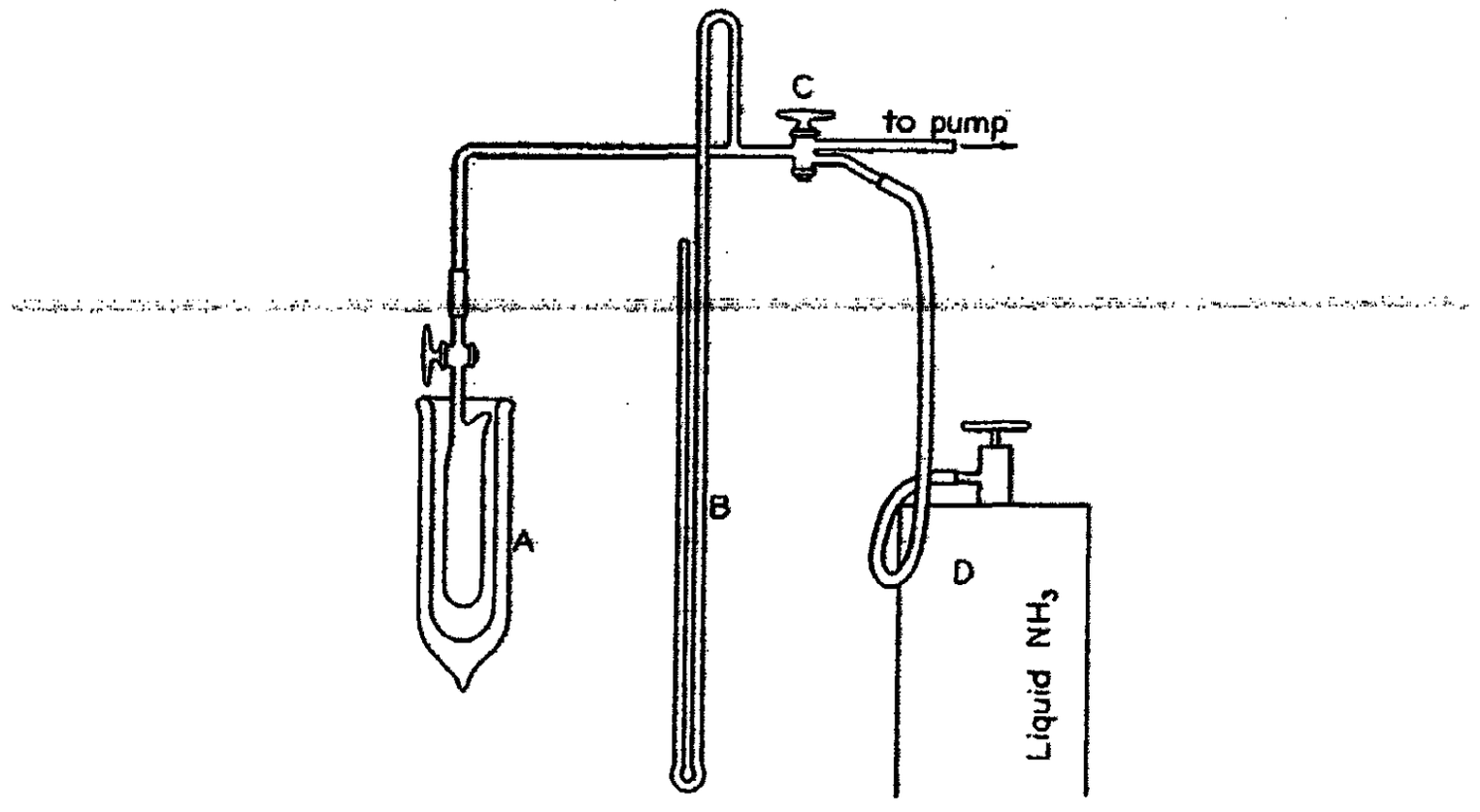


Fig. 3

Removal of the Specimen from the Preparation Tube.—The method of removing these ammono compounds for analysis has heretofore not been published in detail for the reason that the procedure seemed obvious. In view of the fact, however, that experience has shown that such is not the case, it seems worth while to give the details here.

The evacuated tube, *A*, Fig. 4, containing the substance for analysis, and held in any convenient clamp, is connected as shown in the figure with the supply of dilute acid, *B*, which is to serve as solvent. The exterior end of the stopcock tube and the tube connecting with the solvent is completely filled with liquid in order to prevent any access of air to the vessel containing the preparation. On opening the stopcock the acid enters the specimen tube and rests

quietly in the lower end of the tube without coming in direct contact with the substance. This is important in the case of those compounds, and potassium ammonoplumbite is one of them, which explode or decompose with too great violence when brought into direct contact with the solvent. Under the slower action of the vapor of the solvent the salt is gradually hydrolyzed, so that after the lapse of some hours the product may be brought into solution without danger.

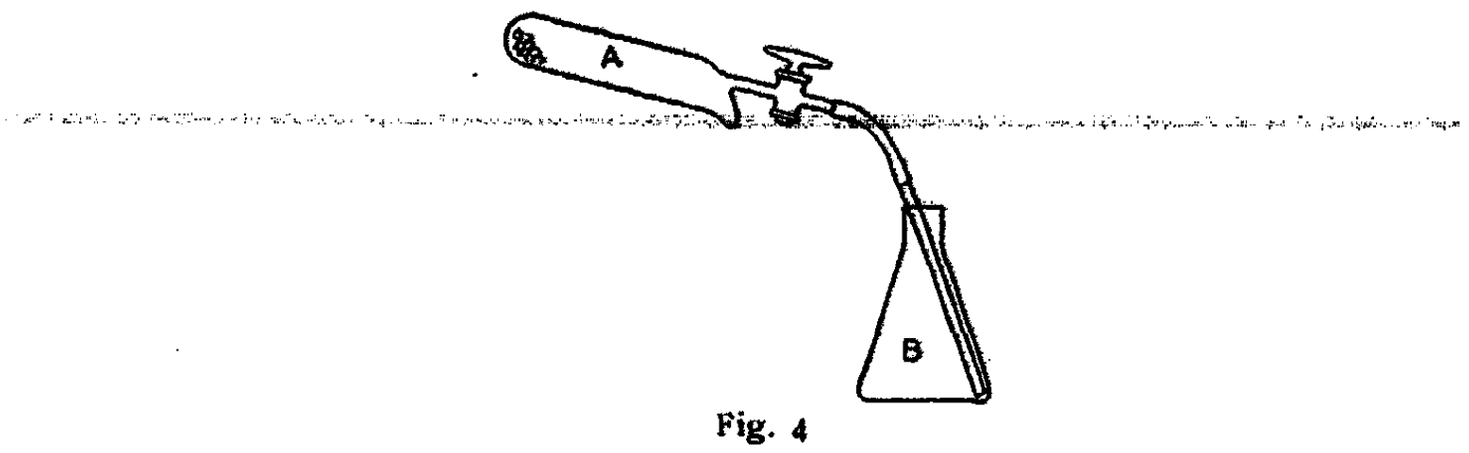


Fig. 4

The preparation tube is then delivered of its contents by means of the arrangement shown in Fig. 5, the manipulation of which is obvious. After washing the tube, it is dried, evacuated and wighed. The weight of the sample for analysis thus becomes known.

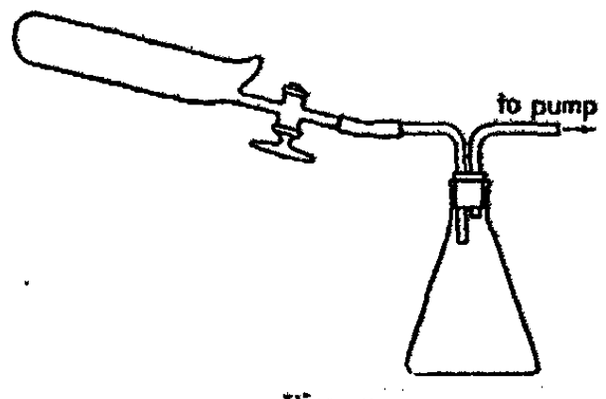


Fig. 5

Analytical Procedure.—From the acetic acid solution obtained as described above the lead is precipitated by means of hydrogen sulphide and weighed as lead sulphide. The filtrate is evaporated to dryness with excess of hydrochloric acid, thus converting the ammonium and potassium acetates

into the chlorides. The ammonium chloride is driven off by ignition, thus leaving the potassium chloride.

Analytical Results.—I. This specimen of potassium ammonoplumbite was recrystallized three times and was dried *in vacuo* at laboratory temperature. One-fourth of 2.8235 grams of the substance gave 0.5615 gram PbS, 0.5905 gram. of mixed NH_4Cl and KCl and 0.1865 gram KCl.

	Calculated for $PbNK.2NH_3$	Found I
Pb	70.4	68.8
N	14.3	15.0
K	13.3	13.8
H	2.0	

II. After five recrystallizations this specimen was dried *in vacuo* at 60°. One-fourth of 2.4232 grams of the substance gave 0.5072 gram PbS, 0.4283 gram of mixed NH_4Cl and KCl and 0.1640 gram KCl.

III. In the preparation of this specimen the lead imide was washed ten times and the potassium ammonoplumbite was recrystallized seven times. The salt dried *in vacuo* at —42° lost 0.0570 gram NH_3 when heated to 20°, and a total of 0.1489 gram NH_3 when heated to 125°. One-half of 1.6419 grams of the salt dried at 125° gave 0.6957 gram PbS, 0.5541 gram mixed NH_4Cl and KCl and 0.2236 gram KCl.

IV. The salt dried *in vacuo* at —40° lost 0.0190 gram NH_3 when heated to 20°, and a total of 0.0539 gram NH_3 when heated to 130°. One-half of 0.5208 gram of the salt dried at 130° gave 0.2225 gram PbS, 0.1769 gram of mixed NH_4Cl and KCl and 0.0769 gram KCl.

V. The salt dried *in vacuo* at —40° lost 0.0389 gram NH_3 when heated to 133°. 0.6459 gram of the salt dried at 133° gave 0.5412 gram PbS, 0.4520 gram mixed NH_4Cl and KCl and 0.1935 gram KCl.

VI. The salt dried *in vacuo* at —45° lost 0.0320 gram

NH_3 when heated to 20°, and a total of 0.0880 gram H_3N when heated to 140°. One-half of 0.9619 gram of the salt dried at 140° gave 0.4108 gram PbS, 0.3350 gram of mixed NH_4Cl and KCl and 0.1323 gram KCl.

VII. In this experiment the preparation tube with its contents, after drying *in vacuo* at —80° in a bath of carbon dioxide and ether, lost 0.0570 gram NH_3 at 20°, and a total of 0.1600 gram NH_3 when heated to 90°. Ammonia was then distilled into the preparation tube and the operation of determining the ammonia of crystallization was repeated. At 20° the salt lost 0.0611 gram NH_3, at 90° a total of 0.1613 gram NH_3. In a second repetition of these determinations it was found that long-continued pumping at —43° brought about a loss of 0.0597 gram NH_3. The total loss at 100° was found to be 0.1595 gram NH_3. The weight of the salt dried at 100° was 1.7200 grams. One-half of this gave 0.7389 gram PbS, 0.5730 gram mixed NH_4Cl and KCl and 0.2345 gram KCl.

Summary.—Calculations of the percentage composition of the salt from the above analytical data give the following results:

	Calculated for $PbNK.NH_3$	Found I			Found II		
Pb	74.7	72.5	73.6	74.1	72.6	73.9	74.4
2N	10.1	11.5	10.5	10.2	10.5	10.5	10.3
K	14.1	14.2	14.2	15.5	14.9	14.4	14.3
3H	1.1						
	100.0	99.3	99.4	100.8	99.1	99.8	100.1
$1NH_3$	6.13	....	5.6	6.5	6.0	5.8	6.0
$1.5NH_3$	9.20	....	9.1	10.1	. .	9.1	9.3

The composition of the crystallized salt is therefore to be represented by the formula, $PbNK.2.5NH_3$, that of the salt dried at 20° by the formula $PbNK.2NH_3$, and that of the salt dried at 100° by the formula $PbNK.NH_3$.

Properties of the Salt.—When a liquid ammonia solution of potassium ammonoplumbite is evaporated the compound separates from concentrated solutions in the form of large, beautifully developed, colorless, transparent crystals having the composition represented by the formula $PbNK.2.5NH_3$. The compound is very soluble at laboratory temperatures; much less so, but still readily soluble at the temperature of a liquid ammonia bath. It possesses conspicuous crystallizing power and its solution shows the phenomenon of supersaturation to a marked degree. It effloresces rapidly when the pressure of ammonia gas in contact with the salt is released. Even at forty degrees below zero the salt gradually loses ammonia to the extent of half a molecule when the pressure is sufficiently low. At higher temperature the salt loses a total of one and a half molecules of ammonia and takes on a very dark chocolate-brown color. The compound thus dried has a composition which is to be represented by the formula, $PbNK.NH_3$, or NH_2-Pb-NHK, or $PbNH.KNH_2$, or possibly by HPb(NH)NHK. An attempt to expel additional ammonia from the salt resulted in the explosion of a specimen at 140°–145°. The salt or its solution is instantly discolored by the action of traces of atmospheric air. It explodes with violence on coming into contact with water or dilute acids. Mere exposure to the atmosphere in several instances led to violent explosions. It is hydrolyzed completely by the action of water vapor.

Summary

An ammonosalt of the composition represented by the formula $PbNK.2.5NH_3$, and named potassium ammonoplumbite has been prepared by the action of the ammono base, potassium amide in solution in liquid ammonia on the amphoteric ammono compound, lead imide, in accordance with the equation,

$$PbNH + KNH_2 = PbNK + NH_3.$$

The salt separates from its solution in liquid ammonia

in the form of beautiful colorless crystals which readily lose successively one-half molecule and one molecule of ammonia, giving products of the composition represented respectively by the formulas $PbNK.2NH_3$ and $PbNK.NH_3$.

Stanford University, California,
March 1, 1911

STUDIES IN THE ELECTROCHEMISTRY OF THE PROTEINS. VII. THE MODE OF FORMATION AND IONIZATION OF THE COMPOUNDS OF PROTEINS WITH INORGANIC ACIDS AND BASES

T. BRAILSFORD ROBERTSON

(From the Rudolph Spreckels Physiological Laboratory of the University of California)

1. Introductory

The investigations of Emil Fischer and of Kossel have shown us that the proteins are built up from amino-acids linked up in a catenary manner, and have demonstrated that the mode of linkage is expressed by the formula:—

—COHN—.

By methods which are too well-known to require description here, Fischer has succeeded in building up chains of amino acids linked together in this manner which he terms "Polypeptids," many of which exhibit characteristic properties of of the peptones, such as precipitability by ammonium sulphate, digestibility by trypsin, etc., and some of which have been found to occur in incomplete protein digests as intermediate products of hydrolysis.

These polypeptids and, presumably, the proteins, are as essentially amino-acids as the amino-acids out of which they are built up. Thus glycylglycin, $NH_2.CH_2.CO.NH.CH_2COOH$ is as typically an amino-acid as glycocoll itself ($NH_2.CH_2.COOH$), since it possesses an NH_2 group as well as a COOH group, and hence is capable of forming compounds both with acids and with bases. On undergoing electrolytic dissociation it may be supposed to yield either hydrogen (H^+) ions, or hydroxyl ions, owing to the occurrence of a reaction with water of the type:

$$R\begin{cases}NH_2\\COOH\end{cases} + H.OH = R\begin{cases}NH_3OH\\COOH\end{cases}$$

just as ammonia, in solution, partially reacts with water to form NH_4OH.

It is usually conceded that these elements in the structure of the proteins afford an explanation of the power which they possess of neutralizing both acids and bases; the "amphoteric" character of the proteins. To this opinion I have also formerly inclined, but an accumulation of data irreconcilable with this view have induced me to abandon it. The weight of evidence appears irresistible that some elements in the protein molecule other than terminal NH_2 or COOH groups are responsible for the acid- and base-neutralizing power which is possessed in such a marked degree by many proteins.

In the first place the investigations of Levites[1] have shown that only a very small proportion of the nitrogen in proteins is present within their molecules in the form of NH_2 groups, and even his estimates of the NH_2 nitrogen are probably in excess of the true values.[2] Now Edestin, as Osborne has shown,[3] is insoluble, when in the free condition, in water. It forms an insoluble hydrochloride containing 14×10^{-5} equivalents of HCl per gram and, on further addition of acid, passes into solution. Its combining capacity for acids does not remain constant, however, for at neutrality to Tropaeolin, which corresponds[4] to a reaction of from 0.01 to 0.001 N H^+, it neutralizes 127×10^{-5} equivalents of acid per gram. Hence, if the acid is neutralized by the $-NH_2$ groups of Edestin, the number of these groups must be at least $\frac{127}{14} = 9$.[5]

[1] S. Levites: Zeit. physiol. Chem., 43, 202 (1904); Biochem. Zeit., 20, 224 (1909).

[2] Emil Fischer: "Untersuchungen ueber Aminosauren, Polypeptide und Proteine" Berlin, 1906, 52.

[3] T. B. Osborne: Jour. Am. Chem. Soc., 21, 486 (1899); Zeit. physiol. Chem., 33, 240 (1901).

[4] Ed. Salm: Zeit. phys. Chem., 57, 471 (1907).

[5] Osborne believes that an insoluble "monochlorhydrate" is also formed, containing 7×10^{-5} equivalents of acid per gram, which would raise this number to 18, but would, at the same time, double the estimate of the molecular weight.

From the former determination it would appear that the molecular weight of Edestin is 7000, and this corresponds with the molecular weight indicated by its tyrosin and glutamic acid content[1] (= 1 mol. tyrosin + 3 mols. glutamic acid + . . .). Nine $-NH_2$ groups in this molecule would correspond to over ten percent of the total nitrogen.[2] From the investigations of Erb,[3] although the exact interpretation which is to be placed upon his results is not perfectly clear, it would appear that the combining-weight of egg-albumin for acids may be as low as 152, while its molecular weight is, according to Hofmeister, 5400 or some multiple of this. Hence, upon the assumption that terminal $-NH_2$ groups bind the acids, there must be at least 35 of them in egg-albumin,[4] which would correspond to no less than 69 percent of the total nitrogen in this protein.

The number of terminal —COOH groups cannot be much in excess of the number of terminal $-NH_2$ groups, since the protein would otherwise be overwhelmingly acid in character[5] and the majority of the proteins possess a distinct capacity for neutralizing acids, even when they are themselves predominantly acid. Now free casein[6] is insoluble in water, but when combined with acids or with bases it is soluble. To carry one gram of casein into solution 11.4×10^{-5} equivalents of base just suffice, indicating a molecular weight, for the casein, of about 8800 or a multiple of this. The tyrosin, glutamic

[1] A. Kossell and A. J. Patten: Zeit. physiol. Chem., 38, 39 (1903).

[2] Or almost exactly to the $-NH_2$ content of the Arginin, calculated as the *free* diamino acid, which the Edestin molecule contains. Kossel: (Zeit. physiol. Chem., 25, 165 (1898) attributes the basic properties of proteins to their content of hexone bases, and to this view electrochemical data lend very decided support. Edestin contains 11.7 percent of arginin, but only insignificant amounts (1.0 percent and 1.1 percent respectively) of lysin and histidin. As at least one of the $-NH_2$ groups of the arginin is almost certainly present in the protein molecule in the *imino* form, it is highly improbable that the acid is neutralized by terminal *amino* groups supplied by the arginin.

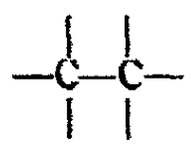
[3] W. Erb: Zeit. Biol., 41, 309 (1901).

[4] Gustav Mann: "Chemistry of the Proteids" London, 1906, 147.

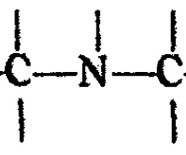
[5] F. Hofmeister: Ergeb. d. Physiol. I Abt., 1 (1902).

[6] T. Brailsford Robertson: Jour. Phys. Chem., 13, 469 (1909); 14, 528 (1910).

acid and sulphur contents of casein indicate a minimal molecular weight of from 4000 to 4400. In the presence of *excess* of base, however, casein attains a maximal combining-capacity (measured by the gas-chain) of 180×10^{-6} equivalents per gram, so that it behaves like a 16-basic acid, and if —COOH groups bind the base there must be 16 of them in the molecule, corresponding to 25 percent of the total oxygen or, almost exactly, *to the number of —COOH groups contained in the glutamic acid radicals in the casein molecule, calculated for the free acid.* In order to provide so many free carboxyls the form of the casein molecule would have to be that of a branched chain, or the radiating spokes of a wheel, at the center of which must exist unions of the type:



and the regular decomposition of this protein into its constituent amino-acids, upon hydrolysis, would be unintelligible.[1] Moreover, in the synthetical polypeptids, which closely resemble the natural peptones in their behavior, the linkage of the amino-acids is not radial but catenary in character[2] and the peptids which have been isolated from the mixed products of partial protein hydrolysis are likewise catenary in structure.

To account for the high acid- and base-containing capacity of the proteins we must therefore look to some other point in the molecule than terminal $-NH_2$ or —COOH groups. The point of union  immediately suggests itself.[3]

[1] Hofmeister: Loc. cit.

[2] Even when dicarboxylic acids enter into the compound. Cf. Emil Fischer and Ernst Koenigs: Ber. d. chem. Ges. Berlin, 37, 4585 (1904); Emil Fischer and Julius Schmidlin: Liebig's Ann., 340, 123 (1905).

[3] It has been pointed out by Vernon (Jour. of Physiol., 31, 346, 1904) that although the power of the sum of the decomposition-products of a protein to neutralize bases is somewhat, yet it is only very slightly greater than that of the unhydrolyzed protein. . Now in the process of hydrolysis the —COH.N— groups of the protein are split into $—NH_2$ and —COOH groups; yet this results in no

The type of this union which occurs in the polypeptids and, presumably, in the proteins is either:

$$—CO.NH— \quad \text{or:} \quad —C(OH) = N—$$

between which, the keto- and the enol-forms, synthetical data do not suffice to decide.[1]

According to Werner's theory of valences the nitrogen in either of these unions contains two latent valences, positive and negative, which, while the nitrogen is trivalent, neutralize one another internally, but which, when the nitrogen becomes pentavalent, are capable, respectively, of neutralizing a negative or a positive radical. The second of the above types of union (the enol-form) carries with it the possibility of the following types of reactions:

$$—COH = N— + Na^+ + OH' = —CONa^{++} + {}''N\begin{matrix}H\\|\\OH\end{matrix} \quad \ldots\ldots(1)$$

and:

$$—COH = N— + H^+ + Cl' = —COH^{++} + {}''N\begin{matrix}H\\|\\Cl\end{matrix} \quad \ldots\ldots(2)$$

yielding, in each case, only *protein* ions.

I have already incidentally dwelt upon the fact that there is reason to suspect that diamino- and dicarboxylic radicals in the protein molecule play a predominant part in accomplishing the neutralization of acids and bases, and electrochemical data, as we shall see, lend most decided support to this view. Accordingly, the above formulae, which represent the reaction when only a single —COH.N— bond is involved,

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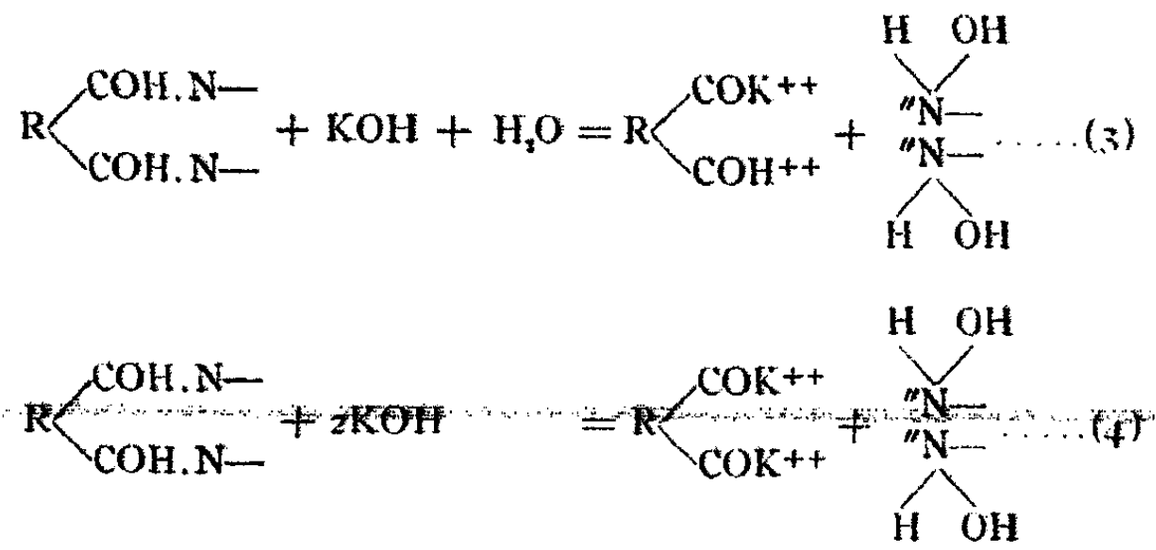
pronounced gain of combining-capacity for bases. The obvious conclusion is that the —COH.N— groups within the protein molecule must be nearly as efficient in accomplishing the neutralization of bases as the —COOH groups of the constituent amino-acids out of which the protein is built up.

[1] Cf. Aders Plimmer "The Chemical Constitution of the Proteins" London, 1908, 2.

should, in reality, be doubled, and the following possibilities exist:

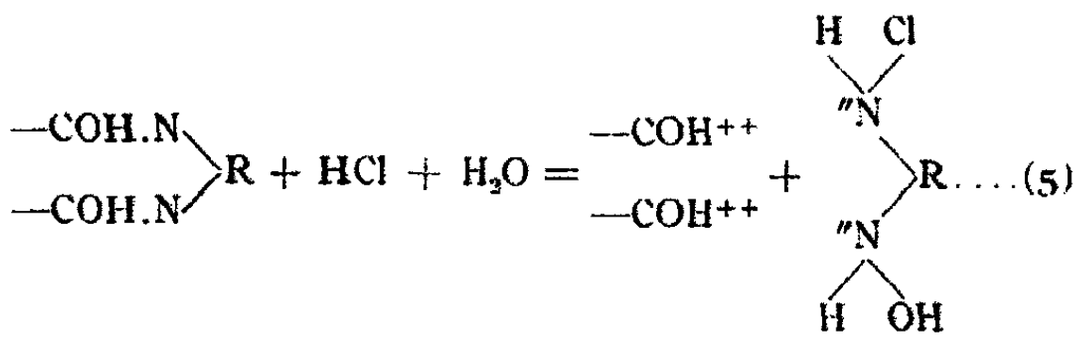
In combination with bases:



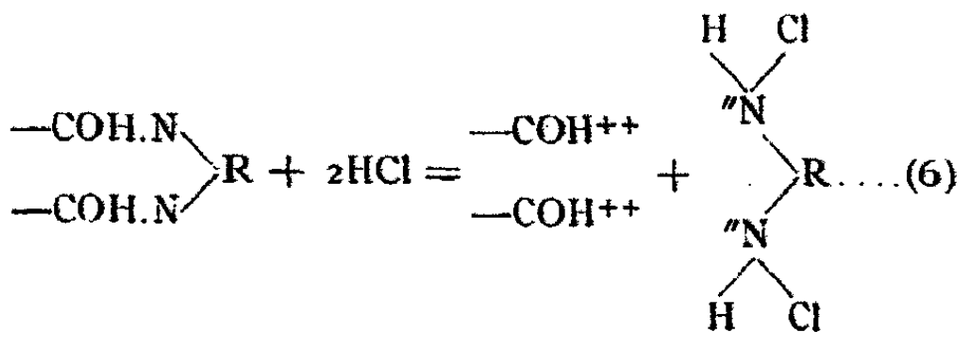
$$R\begin{matrix}COH.N-\\COH.N-\end{matrix} + KOH + H_2O = R\begin{matrix}COK^{++}\\COH^{++}\end{matrix} + \begin{matrix}H & OH\\ \diagdown & \diagup\\ N- & \\ N- & \\ \diagup & \diagdown\\ H & OH\end{matrix} \quad \ldots\ldots(3)$$

$$R\begin{matrix}COH.N-\\COH.N-\end{matrix} + 2KOH = R\begin{matrix}COK^{++}\\COK^{++}\end{matrix} + \begin{matrix}H & OH\\ \diagdown & \diagup\\ N- & \\ N- & \\ \diagup & \diagdown\\ H & OH\end{matrix} \quad \ldots\ldots(4)$$

In combination with acids:



$$\begin{matrix}-COH.N\\-COH.N\end{matrix}\!\!>R + HCl + H_2O = \begin{matrix}-COH^{++}\\-COH^{++}\end{matrix} + \begin{matrix}H & Cl\\ \diagdown & \diagup\\ N & \\ \diagup & \diagdown\\ R & \\ \diagdown & \diagup\\ N & \\ \diagup & \diagdown\\ H & OH\end{matrix} \quad \ldots\ldots(5)$$



$$\begin{matrix}-COH.N\\-COH.N\end{matrix}\!\!>R + 2HCl = \begin{matrix}-COH^{++}\\-COH^{++}\end{matrix} + \begin{matrix}H & Cl\\ \diagdown & \diagup\\ N & \\ \diagup & \diagdown\\ R & \\ \diagdown & \diagup\\ N & \\ \diagup & \diagdown\\ H & Cl\end{matrix} \quad \ldots\ldots(6)$$

It is obvious that in reactions 3 and 5 the molecule of water may or may not participate in the reaction; also that the anionic groups in reactions 3 and 4 may or may not be united to form a single quadrivalent anion (de.ived from a diamino-group) and that the cationic groups in reactions 5 and 6 similarly may or may not be united to form a single quadrivalent cation (derived from a dicarboxylic acid group). As we shall see, no evidence has been found (at least among

the compounds of casein or of serum globulin with bases)[1] for the occurrence of reactions of the type represented by equation 3. Equation 4 faithfully represents, so far as the electrochemical data are concerned, the mode of combination of bases with these proteins, and the anionic groups are united to form one quadrivalent anion. The union of serum globulin and ovomucoid with acids follows equation 5 (with or without the molecule of water) when the concentration of acid is low; but at higher acidities ovomucoid, at least, combines with HCl in the manner indicated by equation 6.

In the following pages I will endeavor to interpret some of the more important electrochemical data published in previous communications of this series, and also certain data not previously published, in the light of the above hypotheses.

2. The Non-ionic Character of the Inorganic Radical in Compounds of Proteins with Inorganic Acids and Bases

In previous communications[2] I have pointed out that the inorganic radical, in the compounds of proteins with inorganic acids and bases, is not electrolytically dissociated as such; basing this conclusion, in the main, upon indirect evidence, *viz.*, that the degree of dissociation of potassium caseinate is not affected by the presence within its solution of KCl, and that the sum of the equivalent ionic migration-velocities of the ions into which the caseinates dissociate is in some instances less than the equivalent migration-velocity of the inorganic radical itself. *Direct* proof of this fact has, however, been obtained by Bugarszky and Liebermann.[3] These observers employed the potentiometric method, using

[1] Unless the fact that the "apparent" molecular conductivity of potassium caseinate (calculated for the molecular concentration of KOH bound by the casein) rises somewhat as the proportion of base to protein declines (Cf. T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910)) constitutes such evidence. As yet, however, I consider it inconclusive.

[2] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907); 14, 528, 601 (1910).

[3] Stefan Burgarszky and Leo Liebermann: Arch. f. d. ges. Physiol., 72, 51 (1898).

two different concentration-chains. The first was the ordinary gas-chain:

Pt saturated with H_2	Acid (HCl)	Base (NaOH)	Pt saturated with H_2
	2	3	4

the potential being measured, first with pure acid in 2, and then with acid plus protein; the difference between the two readings[1] yielding, by computation from the Nernst formula, the number of hydrogen ions bound by the protein. The second concentration-chain was built up as follows:

Hg	HgCl (solid) HCl	NaCl	NaBr, HgBr (solid)	Hg
1	2	3	4	5

and enabled them to estimate, in a similar way, *the number of Cl′ ions bound by the protein.* Now *the number of Cl′ ions bound by a given mass of protein dissolved in dilute HCl was found to be exactly equal to the number of H^+ ions which it binds.* The following data are compiled from those obtained by Bugarszky and Liebermann.

Egg-albumin in 0.05 *N* HCl

Grams protein in 100 cc	Percent of H^+ bound by the protein	Percent of Cl′ bound by the protein
0	0	0
0.4	9.0	10.7
0.8	18.9	20.2
1.6	33.3	38.0
3.2	60.2	64.0
6.4	96.6	76.0

The slight irregularities are, save in the last observation, no greater than might have arisen out of the uncertain magnitude of the correction for the potential between the elements 2 and 3 in the gas-chain.

[1] Less a correction expressing the potential between 2 and 3.

Confirmatory evidence is not lacking. Loevenhart[1] and others have shown that rennet will not coagulate calcium caseinate unless a small amount of a dissociable salt of calcium is present. The calcium bound by the casein itself is not available for this purpose, but if a small quantity of acid be added then a proportion of the calcium is freed from its combination with casein and, if it forms a *dissociable* salt with the added acid, it is able to bring about coagulation.

W. A. Osborne[2] has shown that if ca cium caseinate be placed inside a dialyzing tube which is then immersed in a very dilute solution of mercuric chloride the mercury diffuses into the tube and is there held in an undissociated form, since the concentration of mercury *within* the tube s found, after some time, to considerably exceed that of mercury in the outside fluid.

Rohmann and Hirschstein[3] have shown that solutions of silver caseinate contain no silver ions, since they fail to yield a precipitate on adding sodium chloride.

The most obvious conclusions to be drawn from these results are that the protein-base or protein-acid compounds are not dissociated at all, or else that they dissociate the positive and negative ions of the inorganic constituent in equivalent proportions, *i. e.*, undergo hydrolytic dissociation.

That these assumptions are incorrect, however, is shown by a large number of experimental data, many of which will be found in previous communications of this series, which demonstrate that the protein compounds with inorganic bases and acids are true electrolytes, independent of any

[1] A. S. Loevenhart: Zeit. physiol. Chem., 4, 176 (1904). The statement of van Dam: Ibid., 58, 295 (1908) and 61, 146 (1909), that the extent of coagulation depends upon the quantity of Ca *bound* by the casein is not irreconcilable with Loevenhart's results. As is well known, the calcium bound in casein as calcium caseinate does not suffice to bring about coagulation. A dissociable salt of calcium must also be present. That this salt may combine with the calcium paracaseinate to form a double salt is not at all unlikely. (Cf. T. Brailsford Robertson: Jour. Biol. Chem.

[2] W. A. Osborne: Jour. Physiol., 34, 84 (1906).

[3] F. Rohmann and L. Hirschstein: Beitr. chem. Physiol. und Path., 3, 288 (1902).

hydrolytic dissociation which they may undergo in solution. I will confine myself to two illustrations, Sjöqvist[1] has shown that if egg-albumin be dissolved in dilute hydrochloric acid, as the concentration of albumin is increased, keeping that of the HCl-solution constant, the molecular conductivity (calculated for 0.025 *N* HCl) diminishes until it reaches a constant minimum value, which is attained when about four grams are dissolved in 100 cc of 0.025 *N* HCl. Now the above quoted results of Bugarszky and Liebermann show that in this solution at least 97 percent of the hydrochloric acid is bound by the egg albumin. The observed "molecular" conductivity (= 67 $\times$ 10^{-5}) is at least 7 times greater than could be accounted or by the maximum possible residual of unneutralized hydrochloric acid and must therefore be due to the protein-acid compound.

Solutions of the caseinates of the alkalies and alkaline earths can be obtained which are neutral or even acid to litmus, these solutions therefore contain no free base; nevertheless they are excellent conductors of electricity[2] a 2 percent solution of potassium caseinate which is neutral to litmus possessing a conductivity of between 80 and 90 $\times$ 10^{-5} reciprocal ohms per equivalent of base neutralized at 30° C.[3] That this conductivity is not attributable to associated impurities, inorganic or other, is shown by the following facts:

(1) It bears a definite relation to the amount of base neutralized by the protein.

(2) The conduction of electricity is accompanied by migration of the casein to the anode, and the amount of casein transported to the anode is directly proportional to the quantity of electricity which is transported through the solution.[4]

Similarly, solutions of the serum-globulinates of the alkalies and alkaline earths may be obtained which are neutral to litmus and which nevertheless conduct electricity, the

[1] J. Sjöqvist: Skand. Arch. f. Physiol., 5, 277 (1895).

[2] O. Sackur: Zeit. phys. Chem., 41, 672 (1902); T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907); 14, 528, 601 (1910).

[3] T. Brailsford Robertson: Jour. Phys. Chem., 14, 538 (1910).

[4] *Ibid.*, 15, 179 (1911).

passage of a direct current through the solutions being accompanied by transport of the protein to the anode.[1]

An experiment which demonstrates in a very striking manner the fact that protein salts do not undergo an appreciable amount of hydrolytic dissociation, in solution in water, nor split off the inorganic radical as an ion, is the following: It will be recollected that casein, deprved of its combined base or acid, is insoluble, and that if, to a solution of a caseinate of a base, exactly enough free acid be added (*e. g.*, HCl) to completely neutralize the combined base the free casein is entirely precipitated. Now one gram of ovomucoid[2] combines with 45×10^{-5} equivalents of HCl to form a compound such that less than 1 percent of the acid remains uncombined (as estimated by gas-chain measurements). One gram of casein combines with 90×10^{-5} equivalents of KOH to form a compound such that less than $^1/_2$ percent of the KOH remains uncombined.[3] If, now, these salts were appreciably subject to hydrolytic dissociation, or if they yielded Cl' and K^+ ions respectively, then on mixing two volumes of a solution of the ovomucoid salt with one volume of a solution of the casein salt (each of the same percentage concentration) the K^+ provided by the caseinate would be exactly neutralized by the Cl' provided by the ovomucoid salt and it might be anticipated that free, uncombined casein, would be precipitated. Nothing of the sort occurs, however. If to 25 cc of a 2 percent solution of the casein salt be added 50 cc of a 2 percent solution of the ovomucoid salt the mixture is no more opalescent than its constituent parts and *the conductivity of the mixture is the sum of the separate conductivities of the two protein salts.*[4] If the mixture be allowed to stand in the pres-

[1] W. B. Hardy: Jour. Physiol., 33, 251 (1905).

[2] T. Brailsford Robertson: Jour. Phys. Chem., 14, 709 (1910).

[3] *Ibid.*, 14, 528 (1910).

[4] Conductivity of a 0.5 percent solution of potassium casein to containing 90×10^{-5} equivalents of KOH per gram, at 30°, $= 38.0 \times 10^{-5}$ reciprocal ohms. Conductivity of a 1.0 percent solution of ovomucoid chloride containing 45×10^{-5} equivalents of HCl per gram, at 30°, $= 80.1 \times 0^{-5}$ reciprocal ohms. Sum of these two conductivities $= 118.1 \times 10^{-5}$ reciprocal ohms. Conductivity of a mixture containing the two salts in the above concentrations, at 30°, $= 108.5 \times 10^{-5}$ reciprocal ohms.

ence of toluol for a considerable period at 36°, however, after 24 to 48 hours a marked increase in its opalescence is observed; after two or three days traces of casein begin to be deposited, and after three to four days all of the casein is found to have been precipitated. The precipitation of the casein is accompanied by a marked increase in the conductivity of the mixture, attributable to the setting free of KCl. It is therefore evident that at the beginning the mixture must contain only minute traces of K^+ and Cl' ions and that the protein salts only yield up these ions with extreme slowness.

Only one conclusion is left open to us, therefore, namely, that the salts which proteins form with inorganic acids and bases do not dissociate at the point of union of the inorganic radical with the protein, but elsewhere, *within the protein molecule its lf*, yielding, not an inorganic and a protein ion, but two or more protein ions, in one or more of which the inorganic radical is bound up in a non-dissociable form.

3. The Electrolysis of Protein Salts

It was shown by Hardy[1] in 1899 that if a trace of acid be added to a solution of dialyzed white of egg, modified by dilution and boiling, on passing a direct current through the solution the whole of the protein finally moves over to the cathode, where it is precipitated. If a trace of alkali is added, however, instead of acid, the whole of the protein finally migrates, under the influenc of the current, to the *anode*. He later showed that serum globulin, in solution, behaves similarly.[2] I have shown that if a direct current of about 1 milliampere be led through a solution of potassium caseinate, casein is deposited upon the anode and the amount of casein so deposited is proportional to the quantity of electricity which has traversed the solution.[3]

Under such circumstances, therefore the protein behaves

[1] W. B. Hardy: Jour. Physiol., 24, 288 (1899).
[2] W. B. Hardy: Loc. cit.
[3] Loc. cit.

like the anion or cation of a salt, like the cation when combined with an acid, like the anion where combined with a base.

Here an apparent, but not a real difficulty confronts us in the application of the hypothesis outlined above to the electrolysis of protein solutions. On the basis of this hypothesis the protein should migrate in both directions, the cation when the protein is combined with a base, and the anion, when the protein is combined with an acid, carrying the inorganic constituent with it. At first sight it might appear as if the proteins should be deposited at both electrodes, but not when we look more closely into the matter. In both of the cases just cited the free, uncombined protein is insoluble, while the combined protein is soluble. Consider the electrolysis of a compound of such a protein with a base. The anion[1]

$$\mathrm{R.N''}\begin{matrix}\mathrm{H}\\|\\\mathrm{OH}\end{matrix}$$

will migrate to the anode, and after neutralizing any excess of base which may be present (since the ion obviously, unless the neutralizing capacity of the protein is already fully satisfied, *i. e.*, unless the solution is very alkaline, must contain —COH.N—groups and therefore, like the entire molecule, is amphoteric) must eventually, when the film in immediate contact with the electrode has become saturated with protein, be precipitated as the uncombined and therefore insoluble protein. The case is very different with the cation $\mathrm{R.CONa^{++}}$, for this, on arriving at the cathode, will bring with it an excess of base and the cathode region must become alkaline and, therefore, free protein cannot be precipitated there. Similarly, in the electrolysis of a salt of such a protein with an acid the uncombined protein must be precipitated at the cathode, but not at the anode. If the protein is of such a type that the free protein is soluble, for example ovomucoid, I have observed that no deposition of protein

[1] In all that follows, for the sake of simplicity, unless actual error is involved by doing so, I will consider only one of the two —COH.N— bonds which are actually split in the electrolytic dissociation of protein salts.

occurs at either electrode, but only the evolution of gas, presumably hydrogen at the cathode and oxygen at the anode.

I have shown[1] that the electrochemical equivalent of casein, precipitated from a potassium caseinate solution (neutral to litmus or phenolphthalein) by electrolysis is 0.0242 ± 0.0019 gram per coulomb. Multiplying this by the Faraday constant, 96530, we obtain the weight of casein which transports one atomic charge. This is 2336 ± 183.

Immediately preceding the precipitation of casein at the anode the proportion of casein to base in the film of solution which is in immediate contact with the anode must be that which obtains at "saturation" of the base by casein. Now at "saturation" of a base by casein the proportion of base to casein is 11.4×10^{-4} equivalents per gram.[2] corresponding if, at this reaction, casein combines with only one molecule of base, with the moleculer weight of 8772. If we assume that at "saturation" of the base with casein two, three, or four, etc., molecules of base are bound up in one molecule of caseinate the molecular weight of the casein would be two, three, or four, etc., times 8772. Either of two assumptions may now be made:

(1) The potassium caseinate dissociates into potassium— and casein ions. If this be the case then the weight of the casein anion must be that of the molecule of casein, *i. e.*, a multiple of 8772, and the *valency* of the casein ions must be a multiple of $\frac{8772}{2336 \pm 183}$ *i. e.*, of 3.8 ± 0.3 or, in round numbers, 4.

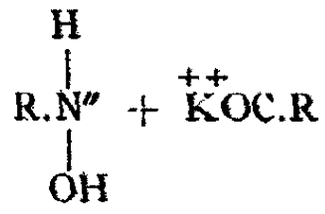
(2) The potassium caseinate dissociates into two protein ions of approximately equal weight. If this be the case then the weight of the casein anion must be half that of the molecule of casein, *i. e.*, a multiple of 4386, and the *valency* of the casein ions must be a multiple of $\frac{4386}{2336 \pm 183}$ *i. e.*, of 1.9 ± 0.15, or in round numbers, 2.

Since, as we have seen above, the former of these two

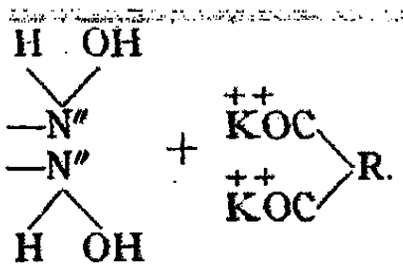
[1] T. Brailsford Robertson: Jour. Phys. Chem., 15, 179 (1911).
[2] *Ibid.*, 13, 469 (1909); 14, 538 (1910).

assumptions is inadmissible, we may conclude *that the valency of the casein ions in solution of a base "saturated" with casein is a multiple of 2.*

This obviously corresponds with the view that the caseinate dissociates into two protein ions according to either of the schemes:



or:



As we shall see, conductivity and freezing-point data point to the latter of these schemes. We may infer that, in all probability, the true molecular weight of the combined casein is about 17600 and that one molecule of the casein is combined with two molecules of a (monacid) base.

4. The Relative Masses of Protein Anions and Cations

From the above experimental results it appears that the masses of the protein cation and anion must be nearly equal, for otherwise the weight of one ion would not be $^1/_2$ but some other fraction of the entire molecule and the valency, deduced from the above experimental data, would not be a whole number but some fraction. Since the valency of an ion is necessarily a whole number and not a fraction, the equivalent weights of the cations and anions which the protein molecule yields must be nearly equal. The above data do not enable us, however, to decide whether or not the weights of the cations and anions are *exactly* equal, since the precision attained in these experiments was not sufficient to reveal with certainty a di erence of less than 10 percent between the weights of the two ions.

It has been shown by Bredig[1] that the equivalent migration-velocities[2] of very heavy ions under unit potential-gradient at constant temperature tend to approach a minimal constant value of about 20×10^{-5} cm per sec. at 18° C. The conception developed above, therefore, of the mode of dissociation of the salts of a protein, leads to the conclusion that the equivalent velocities of migration of both the cation and the anion of a protein salt must be equal. Equal numbers of protein ions must therefore migrate to the anode and to the cathode respectively. Now since only one of these ions is precipitated it would appear possible to determine whether or not they are of equal weight by measuring the change in concentration at the anodal and cathodal regions. Employing Hittorf's method of representation, in the accompanying diagram let the region to the right represent the cathodal and that to the left the anodal region. Let the black dots represent anions and the white cations. The initial state of the solution is represented by the first double row of spots, and its final condition, after the decomposition of six molecules by the current, in the second double row of spots.

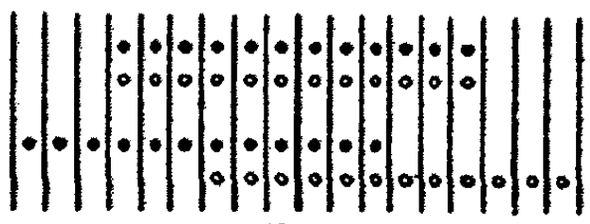


Fig. 1

Since the *velocities* of the ions are presumed to be equal the number of undecomposed molecules of the original caseinate must, after the passage of the current, be the same on each side. The ions which have separated to the left (anions) have been precipitated, while those which have migrated to the right have remained in solution. It is clear from the above

[1] G. Bredig: Zeit. phys. Chem., 13, 191 (1894).

[2] That is, the migration-velocity under unit force. For a divalent ion under unit potential gradient the force exerted is twice as great as that which is exerted on a univalent ion; the *absolute* velocity is therefore twice as great as that of a univalent ion, but the *equivalent* velocity is the same.

diagram that on the right three anions have been lost and three cations have been gained. If they were equal in weight, therefore, it would appear as if the concentration of casein in the right (cathodal) half should remain unaltered by the passage of electricity. A moment's consideration, however, will suffice to show that this is not correct. In attaining this conclusion the assumption has been made that the casein cations, after reaching the cathods, no longer participate in the carrying of current. Unquestionably this is not the case. The combining-capacity of casein increases markedly with increasing alkalinity of its solution, at first in direct proportion,[1] each fresh equivalent of combined alkali splitting another —N.HOC— union. Therefore the potassium or other univalent metal which is transported along with the casein to the cathode, on being transformed there into the hydrate, will split the ion with which it has traveled into two, thus:

$$H_2N.R.COH.N.R.\overset{++}{COK} + {}_2H_2O =$$
$$H_2N.R.COH.N.R.COOH + KOH + H_2;$$

$$H_2N.R.COH.N.R.COOH + KOH = H_2N.R.\overset{++}{COK} + \overset{H}{\overset{|}{''N}}.R.COOH.$$
$$\underset{OH}{|}$$

The resultant cation may be presumed to be retained in the cathodal region while the anion migrates to the anodal region. Each cation which the cathodal region gains, therefore, yields up, provided the masses of the cations and anions are in every case equal, one half its mass to the anodal region again.[2] Referring to the diagram again, therefore, the true gain by the cathodal region will be only half of that represented, equal in weight to only three of the six ions which have been transported to the cathode, while its loss will have been three

[1] T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

[2] This will be rigorously true, of course, only as long as the proportion of base to protein at the boundary of the cathodal region is below that at which the combining-capacity of the protein ceases to increase in direct proportion to the concentration of base, for casein about 100×10^{-3} equivalents per gram.

molecules, together equal to the total weight of caseia lost from the anodal region.[1] Provided, therefore, the anions and cations in a solution of potassium caseinate are equal in weight, no matter what their *absolute* weight, then it is clear that *the loss of casein from the cathodal region must be exactly half the loss from the anodal region.*[2]

I have endeavored to test this theoretical conclusion by determining the loss of casein from the anodal and cathodal limbs of the U-tube employed in the experiments described in my communication upon the electrochemical equivalent of casein.[3] The following are some experimental results. The measurements of the amounts of casein were made by means of the refractometer, as described in the communication to which I have referred.

1. Solution of 3.75 percent in 0.03 *N* KOH neutral to phenolphthalein. Electrolysis for 2 hours at 30°; current approx. 1 milliampere.

Grams of casein lost from the anodal arm	0.062 ± 0.007
Grams of casein lost from the cathodal arm	0.036 ± 0.009
Ratio	1.9 ± 0.7

2. Solution of 4 percent casein in 0.02 *N* KOH; neutral to litmus. Electrolysis for 2 hours at 30°; current approx. 1 milliampere.

Grams of casein lost from the anodal arm	0.093 ± 0.008
Grams of casein lost from the cathodal arm	0.045 ± 0.007
Ratio	2.15 ± 0.55

3. Solution of 3.75 percent in casein 0.03 *N* KOH; neutral to phenolphthalein. Electrolysis for 2 hours at 30°; current approx. 1 milliampere.

Grams of casein lost from the anodal arm	0.070 ± 0.008
Grams of casein lost from the cathodal arm	0.045 ± 0.009
Ratio	1.65 ± 0.55

[1] The anions *returned* to the anode, or their equivalent, are of course deposited on the anode and do not constitute a gain on the part of the anodal region.

[2] The same conclusion may be reached by another process of reasoning. It is evident that the end-result of the return of half of each cation to the anode must be the same as if the cation possessed one half the absolute migration-velocity of the anion. Under such circumstances, the anion being deposited upon the anode and the cation retained in the cathodal fluid, the loss from the anodal region, as a reference to the Hittorf diagram shows, must be half the loss from the cathodal region.

[3] T. Brailsford Robertson: Jour. Phys. Chem., 15, 179 (1911).

Within the experimental error, therefore, the ratio of the anodal to the cathodal loss is 2 as demanded by theory. The experimental error in determining the ratio is large, however, as the above figures reveal, and although these results may be taken as confimatory of the general correctness of the above outline of the mechanism of electrolysis in these solutions, yet they do not suffice to enable us to determine whether or not the protein anions and cations are absolutely equal in mass. Further elaboration and refinement in the technique of these measurements will doubtless in the future enable us to measure the relative masses of the protein anions and cations with considerable precision.

In passing it may be pointed out, however, that these results afford a striking confirmation of the view which I have developed above that the protein salts in solution in water do not yield protein and inorganic ions but only protein ions. Referring to the Hittorf diagram again it will be evident that if the cations were potassium ions the loss of casein from the anodal region should be at least four times that from the cathodal region, since the equivalent velocity of potassium ions is at least four times that of heavy organic ions. The experimental fact that the loss from the anodal region is only about twice as great as that from the cathodal region can only be interpreted by assuming that protein material is transported into the cathodal region by the current, *in other words, that the current is transported in both directions by protein ions.*

5. The Migration-Velocity of Protein Ions

W. B. Hardy endeavored to measure the migration-velocities of serum-globulin ions directly[1] by placing solutions of serum-globulin, combined with acids or bases at the bottom of a U-tube and placing above the solutions, in both arms of the U-tube, a solution of the acid or base employed to dissolve the protein. A potential gradient was placed across the U-tube and it was observed that in acid solutions *both* boundaries of the

[1] W. B. Hardy: Jour. Physiol., 33, 286 (1905).

protein solution migrated towards the cathode, while in alkaline solutions *both* boundaries of the protein solution migrated towards the anode. The rate of migration varied between 7 to 10 $\times$ 10^{-5} cm per sec for unit potential gradient when strong acids or bases (HCl and NaOH) were employed and about 20 $\times$ 10^{-5} cm per sec when a weak acid (acetic acid) was was employed. Following the view which I have developed of the mode of dissociation of protein salts it would appear as if the boundaries should move in *opposite* directions at approximately equal velocities. A moment's consideration of the method of measurement employed by Hardy shows, however, that under the conditions of his experiments this would not occur. At the boundary of the protein solution (nearly neutral) and the HCl solution (for example) a difference of potential of considerable magnitude would exist owing to the much more rapid diffusion of H^+ into the protein solution than of Cl'. This difference of potential would lower the potential gradient at the cathodal boundary and raise it at the anodal boundary. Bearing in mind the fact that the two protein ions are possesssed of the same equivalent migration velocities under unit potential fall, the effect of these inequalities in potential gradient must have been, at the anodal boundary, to urge the protein anions toward the anode more rapidly than the cations were repelled from the boundary, and at the cathodal boundary to repel the protein anions from the boundary into the protein solution more rapidly than the cations crossed the boundary. The net result of these processes would be, obviously, a migration of the protein, as a whole, towards the anode. The contact-differences of potential at the boundaries would be equal in magnitude but opposite in sense and hence both boundaries would migrate at the same velocity, but in the same direction. The fact that the highest velocities were obtained when weak acids (acetic) were employed, in which the difference between the equivalent velocities of the ions (H^+ and acetanion) is greatest, strongly supports this interpretation of Hardy's results. Alkali-globulin, in contact with alkaline solutions would, of course, move as a whole, but

somewhat more slowly (since the difference between the velocity of OH' and that of Na^+ is not so great as that between H^+ and Cl'), towards the cathode. This accords with the experimental observations of Hardy. The velocities measured by Hardy, therefore, do not afford a measure of the migration-velocities of protein ions under a uniform potential gradient.

6. The Non-dependence of the Composition of the Compounds of Protein with Acids and Bases upon the Dilution of their Solutions

The view would appear to be very generally held[1] that the salts which the proteins form with acids and bases are subject in a very high measure to hydrolytic dissociation. This view is nevertheless erroneous. When a base unites with an organic acid to form a salt by the neutralization of a —COOH group the reaction may be expressed as follows:

$$R.COOH + KOH \rightleftarrows RCOOK + H.OH.$$

If the acid is a very strong one then the reaction will proceed completely from left to right and the salt will not be appreciably decomposed by dilution. If, however, the acid is tolerably weak (*e. g.*, acetic acid) so that the water itself, acting as an acid, is able, if present in large proportion, to partially displace it from its combination with the base, then the reaction will not proceed completely from left to right but will pause, in accordance with the mass-law, in a condition of balance, which is shifted to the right by the addition of excess of base and towards the left by dilution. On adding excess of base to a dilute solution of an acid of this type, therefore, more of the base will be observed to be neutralized, while the addition of water, *i. e.*, dilution, will result in partial decomposition of the salt. Similar considerations hold good, of course, for the salts of weak bases. When one examines the evidence which has been brought forward by different observers in support of the thesis that protein salts are subject to hydrolytic dissociation, one finds that it is all of the first kind, that is, con-

[1] Cf. for example H. Ley: Zeit. phys. Chem., **30**, 193 (1899); W. Erb: Zeit. Biol., **41**, 309 (1901); L. von Rhorer: Arch. ges. Physiol., **90**, 368 (1902).

sists in the fact upon the addition of excess of acid or base to an acid or alkaline solution of protein a greater proportion of the acid or base is bound by the protein. From this the somewhat illogical, but natural assumption has been made that the protein salts must exhibit the other characteristic property of salts of weak acids and bases, namely, decomposability by water. The fact that protein will bind more of an acid or a base, the greater, within certain limits, the excess of these reagents, admits of a very different explanation, however, namely the splitting of successive —N.HOC— groups by increasing acidity or alkalinity of the solution, while numerous data contained in previous communications of this series and elsewhere enable us to conclude that water is not able to appreciably decompose the salts of proteins, at any rate the salts which casein forms with bases.

For example, it has been shown by a number of observers[1] by direct titration that the quantity of a base which is bound by one gram of casein at neutrality to litmus (*i. e.*, absolute neutrality) or to phenolphthalein is always the same *whatever the total dilution of the system*. I have been able to confirm this result with considerable precision with the aid of the gas-chain.[2] Also, a survey of the gas-chain measurements enumerated in the communication just cited reveals the fact that the combining-capacity of casein for bases, when it attains its maximum in alkaline solutions, is independent of the dilution. That this should be so in alkaline solution is not surprising, since the excess of alkali might be expected to drive the reaction:

$$R.COOH + KOH \rightleftarrows R.COOK + H.OH$$

over towards the right; but that it is so in absolutely neutral solution, when the concentration of free KOH is evanescently small, is an extremely striking fact.

But, not only is the composition of the caseinate of potassium independent of its dilution in *neutral* solution; it is

[1] Cf. Van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905).
[2] T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

also independent of its dilution in solutions which are pronouncedly acid in reaction. I have shown that for percentages of casein lying between 0.5 and 3.0 the quantity of base which is bound by the casein at "saturation" of the casein with base is 0.000114 C, where C is the percentage concentration. In other words the proportion of base to casein is the same at all these dilutions. Now in these solutions the acidity is about $10^{-5}H^+$. A glance at the formula:

$$R.COOH + KOH \rightleftarrows R.COOK + H.OH.$$

suffices to show that in acid solutions, when the KOH concentration is excessively small and the H^+ concentration large, the tendency to hydrolysis of a salt of the type R.COOK must be exceptionally great, yet potassium caseinate does not reveal this tendency, and the conclusion is forced upon us that potassium caseinate is not formed according to an equation of the above type.

Reverting, now, to the hypothesis which I have advanced regarding the mode of formation of protein salts we see that in the equation:

$$-N.HOC- + KOH \rightleftarrows \begin{matrix} H \\ | \\ -N'' \\ | \\ OH \end{matrix} + \overset{++}{K}OC-$$

no water is involved, and consequently, *the composition of the salt must be dependent only upon the relative concentrations of protein and base and not upon the total dilution.* Similarly in the formation of salts with acids:

$$-N.HOC- + HCl \rightleftarrows \begin{matrix} H \\ | \\ -N'' \\ | \\ Cl \end{matrix} + \overset{++}{H}OC-$$

no water necessarily enters into the reaction. Hence both the dependence of the composition of the protein salts upon the excess of acid or base and its non-dependence upon dilution receive a simple interpretation in the light of this hypothesis.

It will, I think, be clear from the foregoing discussion that the non-dependence of the composition of protein salts upon their dilution is one of the most emphatic proofs which we possess of the fact that terminal —COOH and —NH_2 groups are not responsible for their formation.

7. Data Derived from Conductivity and Freezing-point Determinations

In previous communications I have shown[1] that the caseinates and serum-globulinates of the alka ies and alkaline earths obey the Ostwald dilution-law[2] when expressed in the form:

$$m = \frac{1.037 \times 10^{-2}}{\rho(u + v)} x + \frac{1.075 \times 10^{-4}}{\rho(u + v)^2} x^2,$$

where x is the conductivity in reciprocal ohms, m the equivalent concentration of neutralized base and ρ the number of equivalents of protein salt to which one equivalent of neutralized base gives rise and $u + v$ the sum of the equivalent velocities of the ions of the protein salt. For the caseinates of the alkaline earths (Ca, Ba, Sr) the average value of $\rho(u + v)$ is 38×10^{-5} cm per sec at 30°; for the serum globulinates its value is slightly lower. Now Bredig has shown that the equivalent velocity of heavy ions at 15° is about 15×10^{-5} cm per sec. At 30° this would be some 30 per-cent higher or 20×10^{-5} cm per sec. Provided that one equivalent of base yields one equivalent of protein salt and that the salt dissociates into two protein ions the value of $\rho(u + v)$ should therefore be about 40×10^{-5} cm per sec, which is very close to the value actually observed. For the caseinates and serum globulinates of the *monoacid* bases, however, $\rho(u + v)$ is almost exactly twice as great, and hence

[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907); 12, 473 (1908); 14, 528, 601 (1910).

[2] This does not necessarily imply that these salts dissociate only into *two* ions. The general form of the law for electrolytes which dissociate into n ions is:

$$m = Ax + Bx^n$$

and this relation may be satisfactorily represented by several different values of n.

we must conclude, as I have done in the communications referred to, that one equivalent of monacid base yields *two* equivalents of protein salt. Now the freezing-point depression produced by a solution of a caseinate of a monacid base is almost exactly that of a solution of the same molecular concentration as the neutralized base.[1] Since the caseinate of the monacid bases are very completely dissociated at the dilutions employed (for their conductivities increase but slightly on further dilution) we must conclude that *one molecule of neutralized monacid base yields one ion of caseinate.* The same is readily seen to be true for the caseinates of the diacid bases, when allowance is made for their relatively slight degree of dissociation. For the monacid bases, therefore the mode of reaction with casein must be that represented by equation 4 in the introduction. Hence dicarboxylic acid radicals play the leading part in the neutralization of bases by proteins. In this connection it is of interest to observe that the ratio of the maximum ($= 180 \times 10^{-5}$ equivalents per gram) to the minimum ($= 11.4 \times 10^{-5}$ equivalents per gram) combining capacity of casein for bases[2] is almost exactly equal to the number of glutamic acid radicals in the casein molecule, calculated on the basis of a molecular of weight 17600.

Applying the dilution-formula to the determinations made by Hardy on solutions of serum-globulin combined with 9.318×10^{-5} equivalents of HCl per gram we obtain, by the method of least squares:

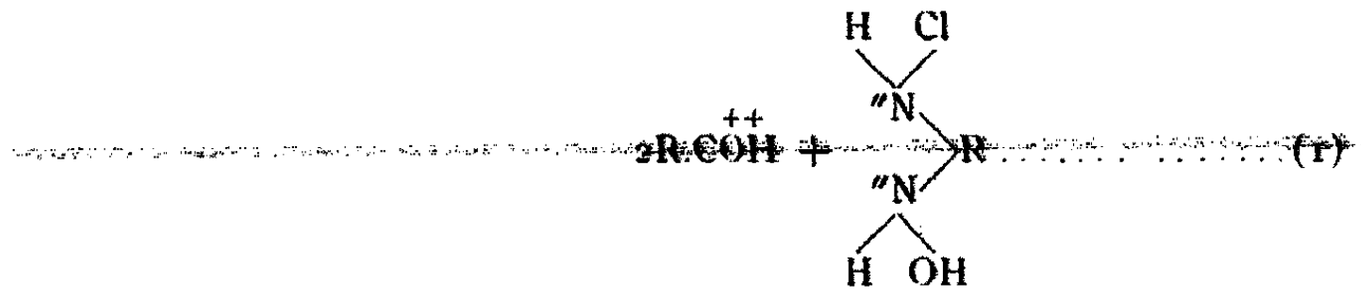
$$\frac{1.037 \times 10^{-2}}{\rho(u+v)} = 7.42 \qquad \frac{1.075 \times 10^{-4}}{\rho G(u+v)^2} = 36964$$

whence $\rho(u + v) = 140 \times 10^{-5}$ cm per sec, or *four* times its value for the globulinates of the diacid bases. I find that solutions of ovomucoid combined with acids (45×10^{-5} equivalents HCl or H_2SO_4 per gram) yield even larger values of $(u + v)$, namely 204×10^{-5} for HCl— ovomucoid

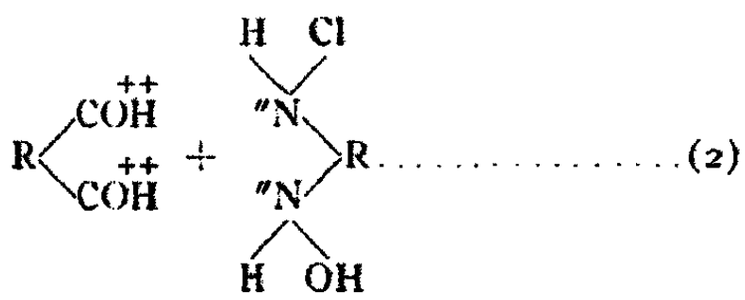
[1] T. Brailsford Robertson and Theo. C. Burnett: Jour. Biol. Chem., 6, 105 (1909).

[2] T. Brailsford Robertson: Jour. Phys. Chem., 14, 528 (1910).

and 189×10^{-5} for H_2SO_4— ovomucoid. Evidently each equivalent of HCl which combines with serum globulin yields *four* equivalents of protein salt and the same is probably true for the salts which ovomucoid forms with acids. Hence the reaction of acids with these proteins is represented by equation 5 in the introduction and the salts themselves (for the proportions of acid to protein named) are represented by either the formula



or the formula:

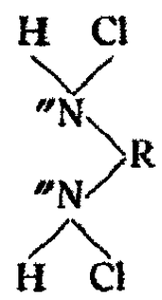


If formula (1) represents the structure of the chloride of ovomucoid which contains 45×10^{-5} equivalents of HCl per gram, then, since this salt is highly dissociated (for the conductivity of its solution increases but slightly with dilution) the freezing-point depression of its solution should be *three times* that of a solution of the molecular concentration of the neutralized acid. If formula (2) represents the structure of the salt then the freezing point depression of its solution should be *two times* that of a solution of the molecular concentrations of the neutralized acid. The experimental fact is that the freezing-point depression of a 0.018 *m* solution of -HCl containing 4 percent ovomucoid (1 g per 45×10^{-5} equivalents) is $0.09° \pm 0.005°$, corresponding to a 0.0055 *m* solution, or almost exactly *three* times the molecular concentration of the neutralized acid.

We may conclude that formula (1) *is that of this chloride of*

ovomucoid, that in the formation of salts of ovomucoid and serum globulin with acids diamino radicals play the leading part, and that, in ovomucoid at least, the diamino radicals are not directly united to both the —COOH groups of dicarboxylic acid radicals.

Continuing the addition of acid (HCl) to the above solution of ovomucoid a remarkable phenomenon is observed, namely, that *doubling the amount of acid in* the solution does not appreciably alter its freezing point[1] and, consequently does not alter the total number of ions per cc of the solution. Evidently, upon further addition of acid the remaining N— of the diamino radical becomes neutralized and the ion:



is formed.

The form of the dilution-law which we should apply to these solutions is therefore:

$$m = \frac{1.037 \times 10^{-2}}{\rho(u+v)} x + \frac{1.115 \times 10^{-6}}{\rho G(u+v)^3} x^3.$$

The following are the experimental data. Ovomucoid was prepared from the whites of eggs in the manner described by me in previous articles.[2] This ovomucoid was dissolved in solutions of HCl and of H_2SO_4 in such proportion that one gram of ovomucoid was introduced into the solution for every 45×10^{-5} equivalents of acid. Such solutions are very nearly neutral (H^+ = about 3×10^{-5}), over 99 percent of the acid being bound by the ovomucoid.[3] These solutions, (containing 4 percent of the protein) were then diluted to the various concentrations employed and the conductivities of the

[1] The freezing-point depression due to *free* ovomucoid is only *one-third* of that of the above solution, namely: 0.03° ± 0.005° for a 4 percent solution.

[2] T. Brailsford Robertson: Jour. Biol. Chem., 14, 709 (1910); Jour. Phys. Chem., 7, 359 (1910).

[3] T. Brailsford Robertson: Jour. Phys. Chem., 14, 709 (1910).

solutions measured at each dilution. The measurements were carried out at 30° in a conductivity vessel of resistance-capacity 0.1949. The following were the results obtained, the conductivity of the distilled water ($= 4 \times 10^{-6}$) having been subtracted from each of the observed conductivities.

TABLE I

Ovomucoid Chloride

Equivalent-molecular concentration of HCl neutralized by ovomucoid	x = conductivity in reciprocal ohms per cc at 30°
0.0180	276×10^{-6}
0.0090	151×10^{-6}
0.0045	80×10^{-6}
0.0023	42×10^{-6}
0.0011	22×10^{-6}

TABLE II

Ovomucoid Sulphate

Equivalent-molecular concentration of H_2SO_4 neutralized by ovomucoid	x = conductivity in reciprocal ohms per cc. at 30°
0.0180	232×10^{-6}
0.0090	131×10^{-6}
0.0045	73×10^{-6}
0.0023	39×10^{-6}
0.0011	21×10^{-6}

Applying the above equation to the results enumerated in Table I we obtain:

$$m = 5.63x + 0.117 \times 10^6 x^3.$$

In the accompanying table the experimental and calculated values of m are compared. In the third column is given the degree of dissociation of the salt, estimated as the ratio of the calculated value of $5.63x$ to the calculated value of m.

TABLE III

Ovomucoid chloride

(45×10^{-5} Equivalents HCl per gram)

$m \times 10^4$ (experimental)	$m \times 10^4$ (calculated)	Degree of dissociation Percent
180	180	86
90	89	96
45	46	98
23	24	100
11	12	100

The same equation obviously applies so nearly to the experimental results obtained with ovomucoid sulphate that it is not necessary to recompute the constants for this salt.

From the value of $\frac{1.037 \times 10^{-3}}{\rho(u + v)}$ for the ovomucoid chloride we obtain:

$$\rho(u + v) = 184 \times 10^{-5}$$

whence, if $\rho = 4$, $u + v = 46 \times 10^{-5}$; which agrees very well with the values previously obtained, with other proteins, for this constant.

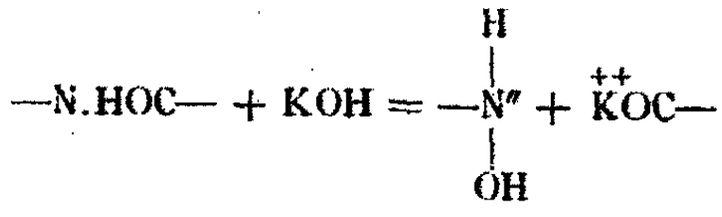
Summing up these results, therefore, we see that *in the formation of the salts of proteins with acids diamino radicals are primarily concerned, while in the formation of the salts of proteins with bases dicarboxylic radicals are primarily concerned.* The correspondence between the diamino-acid content of a protein and its binding-capacity for acids, to which Kessel has drawn attention and that between its dicarboxylic acid content and its combining-capacity for bases, to which I have drawn attention above, is therefore not accidental but, on the contrary, expressive of an essential feature of the union between proteins and inorganic acids and bases.

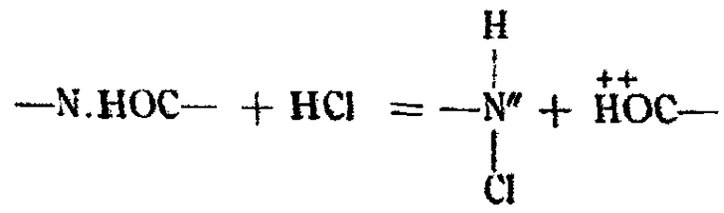
Summary

Data are advanced in support of the views:

(1) That the formation and dissociation of protein salts with inorganic bases and acids are accomplished by the split-

ting of —N.HOC— groups within the protein molecule in accordance with equations such as:





and not by the neutralization of terminal $—NH_2$ or —COOH groups.

(2) That in the neutralization of acids and bases by proteins diamino and dicarboxylic radicals are chiefly involved.

THE PHOTOGRAPHIC PLATE VI

BY WILDER D. BANCROFT

THE LATENT IMAGE. PART II

According to Weisz[1], Scheele in 1777 was the first person to consider that the latent image consisted of metallic silver. This seems a bit far-fetched; but, however that may be, it is certain that the recrudescence of the theory is due to Ostwald[2] and to Abegg.[3] A general outline has already been given[4] and therefore need not be repeated here. Sheppard and Mees[5] say in regard to it:

"Proceeding from the fact that a 'germ' of metallic silver will induce the deposition of further silver upon it from a supersaturated solution, it provides the most satisfactory theory of development, but fails to account for the resistance of the 'latent image' to oxidizing solutions of such potential as to destroy metallic silver. It is also to some extent inconsistent with the initial induction in development."

Weisz[6] claims that the theory is entirely overthrown by the following experiment, carried out in the Leipzig laboratory.

"Luther placed a silver mirror in a glass test tube, placed silver bromide at the bottom of the tube, sealed the tube, and exposed the whole to sunlight. The silver bromide blackened and, at the same time, the silver mirror was attacked, becoming violet in color. It is thermodynamically impossible that in this system metallic silver could be oxidized to silver bromide at the same time that identical silver bromide was changing to identical metallic silver. Therefore the black product, formed from silver bromide by the action of light, cannot be ordinary silver."

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[1] Zeit. phys. Chem., 54, 311 (1906).
[2] Lehrbuch der Allgemeinen Chemie, 2nd. Ed., 2, 1078 (1893).
[3] Archiv. wiss. Photographie, 1, 268 (1899).
[4] Namias: Jour. Phys. Chem., 15, 351 (1911).
[5] Theory of the Photographic Process, 199 (1907).
[6] Zeit. phys. Chem., 54, 311 (1906).

The thermodynamic impossibility does not exist unless the intensity of light were the same at the silver mirror and at the silver bromide. While this may have been the case, the fact that Weisz does not mention it shows that he, at any rate, did not appreciate the importance of it. The following hypothetical experiment will illustrate the point. We take a test tube and fill it half full with anhydrous sodium sulphate. On top of this we place a layer of hydrated sodium sulphate, and we then seal the test tube. If we heat the upper part of the test tube gently, water will distil from the hydrated to the anhydrous sodium sulphate and hydrated sodium sulphate will be changed to anhydrous sodium sulphate at the same time that identical anhydrous sodium sulphate is being changed into hydrated sodium sulphate.[1]

While Luther's conclusion is undoubtedly right, the experiment, as described, does not prove anything. The strongest arguments against the theory of a silver nucleus are to be found in the behavior to reagents, and in the electromotive force measurements. As it will be better to consider these points in connection with the theory that the latent image consists of a sub-bromide of silver, we will take up that hypothesis now.

The most ardent advocate of the subhalide theory is Eder. In a recent paper on the latent image[1] he says:

"In spite of many investigations we do not know definitely what is the nature of the latent image which can be developed with a photographic developer. The bulk of the evidence favors the so-called subhalide theory, which was first suggested more than half a century ago.[3] It has been attacked repeatedly and has recently been defended by me[4] at different times. According to this theory a short exposure causes silver bromide (AgBr) to lose a small amount of bromine

[1] Cf. Goldstein: Jour. Phys. Chem., 13, 50 (1909).

[3] Eder: Akad. Wiss. Wien., 114, IIa, 1159 (1905).

[3] In 1843 Choiselat and Ratel assumed the existence of silver sub-iodide in the latent daguerreotype image.

[4] Eder's Jahrbuch der Photographie, 14, 80 (1900).

so that there is formed one or (as I believe) more silver subbromides (Ag_xB_{x-y}) of unknown atomic composition. Luther assumes the existence of a single subhalide, the subbromide (Ag_2Br), or the subchloride (Ag_2Cl), and believes that the latent image and the salt blackened by light contain the same substance (Ag_2Br or Ag_2Cl as the case may be) though in different relative amounts. Luther[1] considers it improbable that we have a series of solid solutions between Ag_2Br and AgBr Others (Carey Lea, E. Baur,[2] Gunther) look upon the silver chloride (or bromide), which has been changed by light, as a solid solution of halide and subhalide which becomes darker as the exposure to light is increased.

"We call attention to the fact that these theories postulate the formation of some kind of subhalide on exposure to light, though the amount of bromine set free in the formation of the latent image is so small that it cannot be weighed."

Though it is impossible to separate the material forming the latent image from the remaining silver bromide, attempts at analysis have been made in other ways. Luther[3] showed that the oxidation of silver to silver chloride by chlorine was a reversible one. He then placed a weighed amount of silver powder in tenth-normal hydrochloric acid, and added measured quantities of chlorine water, shaking the vessel so as to bring about equilibrium. After each addition of chlorine water he placed a platinum electrode in the solution and measured the potential against a silver-plated platinum electrode in a tenth-normal hydrochloric acid solution containing an excess of silver halide. In Table I are given the equivalents of chlorine per hundred equivalents of silver, the electromotive force of the cell, the single potential on the assumption that the value for the constant electrode is —0.55 volts, and the time of shaking.

[1] Zeit. phys. Chem., 30, 680 (1899).
[2] Ibid., 45, 518 (1903).
[3] Ibid., 30, 628 (1899).

TABLE I

Equivalents Cl per 100 equiv. Ag	E. M. F. of cell[1]	Single potential	Time of shaking
0	0.00	—0.55	——
10.1	0.02	—0.57	8 hours
23.0	0.04	—0.59	16 hours
34.3	0.06	—0.61	4 hours
45.1	0.08	—0.63	20 hours
55.1	0.96	—1.51	2 days
64.8	0.96	—1.51	5 days
75.3	0.92	—1.47	10 days
85.4	0.84	—1.39	14 days
93.6	0.90	—1.45	22 days
105.0	1.06	—1.61	10 days

It is quite clear from these data that there is a sharp break at the points corresponding to the composition Ag_2Cl and another at AgCl. What further conclusions we are to draw from these data depends on the accuracy which we attribute to them. Luther considered that the values 1.51, 1.51, 1.47, 1.39, 1.54 might be considered as accidental fluctuations round a mean value of 1.45 volts and he therefore drew the conclusion that the solid phases in the system, silver and chlorine, are silver, silver subchloride (Ag_2Cl) and silver chloride (AgCl). He was confirmed in this view by the fact that he obtained precisely similar results with silver and bromine. The data are given in Table II, the measurements being made against a standard silver-plated electrode in a tenth-normal solution of hydrobromic acid to which an excess of silver bromide had been added.

These results show the existence of a solid phase having a composition corresponding to the formula Ag_2Br. For compositions lying between Ag_2Br and AgBr, the data are just as unsatisfactory as in the case of silver chloride. Luther also determined the potential of a platinum electrode in tenth-normal hydrochloric acid to which had been added an excess of ordinary silver chloride and of silver chloride which had been blackened by light. The value of the single potential

[1] The standard electrode is the anode.

TABLE II

Equivalents Br per 100 equiv. Ag	E. M. F. of cell[1]	Single potential	Time of shaking
0	0.0	—0.40	——
12.6	0.0	—0.40	5 hours
25.2	0.0	—0.40	6 hours
37.7	0.0	—0.40	16 hours
50.3	0.0	—0.40	5 hours
56.8	0.76	—1.16	24 hours
62.8	0.86	—1.26	3 days
69.1	0.80	—1.20	5 days
75.2	0.74	—1.14	14 days
87.7	0.76	—1.16	21 days
106.1	0.94	—1.34	14 days

was —1.44 volts which agrees admirably with the hypothetical mean of —1.45 volts calculated from Table I.

This seems conclusive as to the existence of Ag_2Cl as the only solid phase between silver and silver chloride. The values for the different reactions in tenth-normal hydrochloric acid therefore become:

$$E(Ag \longrightarrow Ag_2Cl) = -0.55 \text{ volt}$$
$$E(Ag_2Cl \longrightarrow AgCl) = -1.45 \text{ volt}$$
$$E(Ag \longrightarrow AgCl) = -1.00 \text{ volt.}$$

Unfortunately, further investigations in Luther's own laboratory threw doubt on these conclusions. Baur[2] repeated Luther's work substituting colloidal silver for silver powder and determined the potentials at the end of six months. His experiments were made in a normal instead of a tenth-normal chloride solution and his results are given in Table III.

TABLE III

Equivalents Cl per 100 equiv. Ag	Single potential	Equivalents Cl per 100 equiv. Ag	Single potential
43.5	—0.551	72.9	—0.863
55.5	—0.819	75.2	—0.863
65.4	—0.837	83.2	—0.880

[1] The standard electrode is anode.

[2] Zeit. phys. Chem., 45, 613 (1903); Eder's Jahrbuch der Photographie, 18, 609 (1904).

Weisz[1] comments on these data as follows:

"If we assume that equilibrium has not been reached even after so long a time, these figures give the lower (less oxidizing) limit of the true equilibrium values, always supposing that these are not affected in an uncontrollable way by secondary reactions at the electrodes or by the previous history of the electrode.

"Baur tried another way of determining the same potentials. To the colloidal solution of the photochloride he added an excess of an oxidizing agent having a known potential. The oxidizing agent is reduced while the subchloride is oxidized to chloride and an equilibrium is reached. With a ceric and cerous solution, for instance, as oxidizing agent, this corresponds to the reaction.

$$Ag_2Cl + Cl' + Ce^{\cdots} \rightleftarrows 2AgCl + Ce^{\cdots\cdot}.$$

On the assumption that equilibrium occurs before the colloidal photochloride solution coagulates, an electrode dipped into the solution will show the easily measurable potential of the ceric and cerous solution, which is identical with that of the potential $Ag_2Cl/AgCl$.

"Baur used a ceric and cerous solution, a chromate and chromic solution, and a ferric and ferrous solution His solutions were kept normal with respect to potassium chloride." The data are given in Table IV.

TABLE IV

Equivalents Cl per 100 equiv Ag	Single potentials		
	Ce^{IV}	Cr^{VI}	Fe^{III}
55	—0.890	—0.900	—
62	—0.920	—0.910	—0.917
75	—0.926	—0.910	—
82	—0.936	—0.920	—0.917
90	—	—0.960	—
95	—1.012	—0.960	—0.935

[1] Zeit. phys. Chem., 54, 314 (1906).

"If we assume that equilibrium was not reached before coagulation and that an excess of the oxidizing agent was therefore present, these give the upper (more oxidizing) limit of the true equilibrium values."

These data lead to the following values for the different reactions in normal chloride solution:

$$E(Ag \longrightarrow Ag_2Cl) = -0.55 \text{ volt}$$
$$E(Ag_2Cl \longrightarrow AgCl) = -0.8\text{–}9 \text{ volt}$$
$$E(Ag \longrightarrow AgCl) = -0.7 \text{ volt}.$$

These values and those in Table III are quite different numerically from the ones obtained by Luther. What is more serious is that these values in Table III and IV show a steady increase as the chlorine content increases. If these results are correct we have a series of solid solutions, presumably running from Ag_2Cl to AgCl.

There is no certainty even about this because Heyer's work in Luther's laboratory points to the following set of values when the chloride solution is hundredth-normal:

$$E(Ag \longrightarrow Ag_2Cl) = -0.67 \pm 0.05 \text{ volt}$$
$$E(Ag_2Cl \longrightarrow AgCl) = 0.65 \pm 0.05 \text{ volt}$$
$$E(Ag \longrightarrow AgCl) = -0.66 \text{ volt}.$$

Since these sets of values refer to three different concentrations, they have been recalculated by Weisz[1] to the arbitrary chloride concentration of 10^{-5} which is supposed to be the value for the solubility of silver chloride in pure water.

TABLE V

	Luther	Baur	Heyer
$E(Ag \longrightarrow Ag_2Cl)$	−0.78 volt	−0.84 volt	−0.84 volt
$E(Ag_2Cl \longrightarrow AgCl)$	−1.68 volt	−1.14 volt	−0.82 volt
$E(Ag \longrightarrow AgCl)$	−1.23 volt	−0.99 volt	−0.83 volt

Weisz comments on the results as follows:

"Luther's values are unquestionably too high. This is natural when one considers that Luther chlorinated silver

[1] Zeit. phys. Chem., 54, 318 (1906).

powder while Baur used colloidal silver. In view of the great slowness with which chlorine reacts after there are fifty equivalents of chlorine per hundred of silver 'Ag_2Cl', the values obtained with colloidal silver are the more reliable because colloidal silver reacts more readily. Beyond the break in the curve it is probable that Luther did not measure equilibrium concentrations of chlorine.

"Though Baur's data are unquestionably more nearly right than Luther's, it is probable that they are too negative. It seems probable that Baur's upper values (Table IV) are too negative because he did not keep out the oxygen of the air. A potential of —0.917 corresponds to a ferric and ferrous solution in which the ratio of ferrous to ferric is 40 to 1. When the oxygen of the air is not excluded, it would be very difficult to reach lower concentrations of the ferric salt. The importance of the changes which indicate the existence of solid solutions is not affected by this, because all the experiments were made in the same way and any errors would have the same effect in all cases.

"Baur's lower values are somewhat uncertain because they were obtained after the solutions had stood in contact with platinum electrodes for half a year. After so long a time the previous history of the platinum electrode may make itself felt in a way for which no correction can be made. Baur's potentials do not harmonize with the following well-known fact. Silver chloride is not reduced in the slightest by ferrous sulphate. The potential of the ferrous sulphate solution may be taken as about —0.9 volt when it is prepared without any special precautions. With Baur's value of —1.24 volt for E ($Ag_2Cl \longrightarrow AgCl$) silver chloride should be reduced by ferrous sulphate to silver subchloride.

"Heyer's measurements are the only ones which agree with the potential usually obtained for a silver electrode in a solution containing silver as ion; with the conductivity measurements; and with the value for the solubility of silver chloride. It therefore seems that the true values for the potentials in question lie very close together and that Hey'ser

values are nearer the true ones than are Baur's If the three potentials are nearly the same, it means that room temperature is very close to the one at which silver, silver subchloride and silver chloride can occur as coexistent phases. It is not possible therefore to decide the question of the latent image definitely by means of potential measurements. Nevertheless the existence of the subchloride follows from the change in the reaction velocity at the break in the curve (Luther, Baur, Heyer) and from the discontinuity of certain properties at the same point (color-sensitiveness, Baur)."

Some of Heyer's chemical experiments are interesting.[1]

"When freshly reduced silver is prepared by reduction of silver nitrate with formaldehyde and sodium carbonate, it is oxidized practically completely to silver chloride or silver bromide by different chlorinating agents (ferric and ferrous chloride solution, chlorine in tenth-normal hydrochloric acid) or brominating agents ($NaOH + Br_2$, $KOH + Br_2$, $NaCl + Br_2$, $H_2SO_4 + Br_2$). There is a difference, however, in the rate of chlorination or bromination between the beginning and the end of the reaction. According to Luther's preliminary observations, oxidizing agents with potentials between —0.55 and —0.1 volts should oxidize silver only to subchloride. Heyer obtained chloride however under these conditions.

"Heyer prepared subchloride by Guntz's method, heating silver subfluoride with phosphorus trichloride in a sealed tube to 140°. He tried to find a characteristic reaction which would distinguish between the subchloride and a mixture of silver and silver chloride in a molecular ratio of one to one. The nearest that he came to one was that nitric acid at first dissolves the excess of silver readily from Guntz's subchloride whereas strong nitric acid (sp. g. 1.2) does not dissolve any silver when the excess of silver over that required for silver chloride has been reduced to one to two percent. The specific gravity of Guntz's subchloride (6.76) is very close to that of a molecular mixture of silver and silver chloride (6.91).

[1] Cf. Weisz: Zeit. phys. Chem., 54, 316 (1906).

"Most of Heyer's experiments dealt with the effect of definitely varied oxidizing or reducing agents upon Guntz's subchloride, upon silver, and upon silver chloride. In harmony with the experiments on silver, Heyer found that a ferric and ferrous chloride solution with a potential of —1.0 volt oxidized Guntz's subchloride to chloride. *This oxidation takes place very slowly.* The subchloride had taken up scarcely one-sixth of the possible amount of chlorine after having been shaken for twenty days. These experiments are in harmony with Baur's value of —0.85 volts for E ($Ag_2Cl \longrightarrow AgCl$) but not with Luther's value of —1.45 volt. On the other hand *silver is oxidized rapidly to silver chloride by a ferric and ferrous chloride solution having a potential of —1.0 volt.* The reaction is complete in two days.

"When silver was shaken for five days and a half with a solution, fiftieth-normal with respect to chloride and containing an oxidizing agent having a potential of —0.66 volt, over half the silver (Ag : Cl = 1 : 0.73) was chlorinated. When silver chloride was shaken for six days with a solution, hundredth-normal with respect to chloride and containing an oxidizing agent having a potential of —0.62 volts, more than half of the silver chloride (Ag : Cl = 1 : 0.26) was reduced to silver. The oxidizing agent was a ferric and ferrous acetate solution, and the results are the mean of two limiting series. When referred to hundredth-normal chloride solutions, this means that

$$Ag + 0.01\ Cl' - 0.68 \text{ volt} \longrightarrow AgCl$$
$$AgCl + 0.01\ Cl' - 0.64 \text{ volt} \longrightarrow Ag.$$

Somewhere between —0.64 and —0.68 volt is the potential at which silver and silver chloride can coexist in presence of a hundredth-normal chloride solution." From these data, Weisz calculates the values already given, Table V, in the discussion of the figures of Luther, Baur, and Heyer.

Weisz's views in regard to the latent image are summed up in the following paragraphs.[1]

[1] Weisz: Zeit. phys. Chem., 54, 319 (1910).

"The agreement between the observations of Heyer and of Baur is of importance for the question of the latent image. Heyer found that the last one or two percent of the excess of silver in Guntz's subchloride is only removed very slowly even by strong nitric acid. Baur noticed the same thing with his photochloride plates. This is in accord with the observations of Carey Lea, with the usual statements that the latent image is not destroyed by nitric acid, and with my own experiments on plates containing no binder. I found that the visible blackening and the latent image are not changed by being soaked for an hour in nitric acid (sp. gr. 1.4); also that there is no sign of any bleaching when the plates are left for five weeks in a solution containing 20 percent ammonia iron alum, 20 cc conc. H_2SO_4 per 100 cc solution, and a trace of silver as ion. This confirms the earlier experiments of Luther and contradicts a statement by Wetzlar to the effect that the bleaching is complete under these circumstances.

"This is the present status of the question as to the nature of the latent image. When we take account of all the facts, we come to the following conclusion. There are compounds of the type of silver sub-bromide. The latent photographic image consists of a solid solution of subhalide or silver in silver halide. This solid solution contains only small amounts of silver subhalide (or silver) and is very resistant to oxidizing agents."

While this conclusion may be correct, it is not justified by the evidence. The fact that the last excess of silver is not removed readily by contact with nitric acid is not inconsistent with there being a continuous series of solid solutions running from Ag_2Br to AgBr or from Ag_2Cl to AgCl. We should be in a better position to judge as to the facts if we knew the limiting concentrations which are not attacked by more dilute nitric acid (sp. gr. 1.20 or 1.10).

Lüppo-Cramer has defended nearly every point of view at one time or another and he is always interesting though not always convincing. I therefore quote from him at great length.[1]

[1] Lüppo-Cramer: Phot. Correspondenz, 38, 145 (1901).

"For many years there had been no discussion of the fundamental problem of photography, as to the nature of the latent image. The reason for this was that the subhalide theory seemed to satisfy all the theoretical and technical requirements. The recrudescence of the 'silver germ' theory in 1899 caused many investigators to make new experiments. The result of this was that Eder overthrew all the arguments brought forward by the 'silver germ' theorists, and reinstated the old sub-bromide theory.

'Any hypothesis, which is not well founded and which therefore has no right to the title of a theory may to a certain extent retard the progress of science in case its real character is not understood. It is therefore dangerous to be absolutely satisfied with the sub-bromide theory. Since the conflict between one hypothesis and another is always helpful even when the new hypothesis is no better than the old one, the newly-revived 'silver germ' theory has been useful in causing all the old arguments for and against to be tested, and in causing new arguments to be brought forward on both sides. Our literature has thereby been enriched with a new series of important experiments and it has been made clear to those scientific men, who did not trouble themselves about the nature of the latent image, that our theoretical views as to the reactions involved in the production of a photograph are as defective as the technical part of the process is perfect.

"It is not my intention to discuss the 'silver germ' theory again or even to attack the subhalide theory. On the other hand some experiments have brought home to me how little value our previous arguments had either for or against these two hypotheses and consequently I consider it desirable to present these results now.

"The chief support for the silver germ theory was to be found in the experiments in which metallic silver was kept in contact with silver bromide during the development. The old experiment with silver wire was shown by Eder not to be conclusive because the reaction does not take place unless pressure is applied, so that the wire merely produces

an ordinary pressure fog. The so-called contact experiment has been repeated in various forms by the upholders and the antagonists of the silver-germ theory, using silver powder or moist silver which had been reduced by metol.[1] These experiments gave very uncertain results and negative results proved nothing because the grain of the silver was relatively very coarse and it was quite possible that a finer metal would cause the reduction to take place.

"The finest metallic silver known to us is unquestionably the precipitate obtained when making a Lippman color photograph, because here it is essential that the size of the grain shall be of the same order as the wave-lengths of light. I therefore prepared a Lippmann silver bromide emulsion and from that obtained by reduction a silver which we will henceforth designate as 'grain-less' silver. A solution containing 10 g gelatine, 150 cc water and 3 g silver nitrate at a temperature of 40° was poured into a solution containing 10 g gelatine, 150 cc water and 2.5 g potassium bromide. A bluish opalescent liquid is obtained which is reduced by means of a solution containing 10 g crystallized sodium sulphate, 100 cc water 1g hydroquinone, 5 cc ammonia (sp. gr. 0.91). Reduction takes place immediately and at the end of ten minutes, there is added to the dark-brown, but really transparent, emulsion 10 cc glacial acetic acid so as to check any further action of the oxidation products of the developer on the gelatine. The emulsion is poured on ice and allowed to solidify. It is then cut up in the usual way and washed for twenty-fours hours in running water to remove the last trace of soluble products.

"In order to be certain that silver and gelatine were the only substances in the emulsion and that all oxidation products of the developer and all reaction products of the gelatine had been removed, I reduced with iron oxalate a silver bromide emulsion made in exactly the same way. Fifteen grams of potassium oxalate were dissolved in 75 cc water and added to a solution of 5 g iron vitriol in 25 cc water. The reduction

[1] Eder's Jahrbuch der Photographie, 14, 83, 84 (1900).

with iron takes place much more slowly than the reduction with hydroquinone but is finished at the end of an hour. After twenty-four hours washing, traces of iron could still be detected after the gelatine had been destroyed with sulphuric acid. Since basic ferric salts were probably present, the silver emulsion was melted again, treated with 5 cc dilute sulphuric acid (1 : 5), allowed to solidify, and then washed for twenty-fours hours. After this treatment, the emulsion was found to contain no iron.

"In this way, I obtained two kinds of grainless silver and I tested their action on a highly sensitive silver bromide gelatine emulsion. To an amount of silver bromide emulsion containing 5 g AgBr, I added 5 cc of the silver emulsion. This corresponds to 0.04 g metallic silver. The plates were then tested both wet and dry. In order to check the results, I exposed simultaneously one straight plate and two to which silver had been added. One of the plates containing silver was fixed at once while the other was developed together with the control plate. Even in this very finely divided form the metallic silver had no effect on the silver bromide emulsion; the amounts of silver on the two developed plates differed only by the amount of silver added to the one plate, as shown by the experiment with the plate to which silver had been added and which was fixed at once. Since no difference could be detected between the action of silver reduced by hydroquinone and silver reduced by iron, we are justified in considering that there was nothing else in the emulsion than silver and gelatine.

"My next experiment was to convert the grainless silver into sub-bromide by direct bromination. I added 0.6 g bromine in the form of a one percent aqueous solution to an emulsion of grainless silver corresponding to 2.5 g $AgNO_3$. In order to keep track of the color changes in the reddish brown silver emulsion, the bromine water was added in 20 cc lots. After five minutes a sample was taken and examined by daylight. (As a precautionary measure the bromination was carried out in the dark room.) The color passes through

several shades which are hard to describe and finally becomes a reddish violet.

"Although, the emulsion now contained two equivalents of silver to one of bromine, that does not prove that sub-bromide was actually formed. On the other hand, it might be assumed that this hypothetical substance had been formed to some extent. Otto Vogel's method[1] of preparing the sub-bromide by means of cuprous bromide does not seem a promising one to carry out in gelatine owing to the great difficulty of removing the copper completely from the emulsion. The results of Waterhouse's repetition of Vogel's experiments were also not encouraging. However, I applied to my bromination product the tests which Vogel recommends for the sub-bromide. In thiosulphate the substance dissolves partially and the color changes essentially, going over into the shade characteristic of the silver emulsion. This may mean the splitting of the sub-bromide into metal and sub-bromide. Addition of potassium ferricyanide to the thiosulphate caused the solution to clear at once.

"In order to get some idea whether the bromine had reacted anywhere near quantitatively with the silver emulsified in the gelatine, a second equivalent of bromine was added to a portion of the brominated emulsion which already contained one equivalent of bromine to two of silver. If the reaction had taken place quantitatively, this further addition of bromine ought to have caused a complete conversion to silver bromide. This was not the case and it was necessary to add about fifty percent more bromine than the theory calls for before all the silver was converted into the light silver bromide which is completely soluble in sodium thiosulphate. The aromatic odor of the brominated emulsion is a further proof that a part of the bromine had reacted to form organic compounds.

"For the experiments on the hypothetical sub-bromide I used the product obtained by adding the theoretical amount of bromine and also the dark steel-blue product obtained by

[1] Phot. Mittheilungen, 36, 334 1899).

adding fifty percent more bromine. If the sub-bromide is a substance which can be made by chemical reactions, some of it ought to be present in these products containing such different amounts of bromine. Since the first series of experiments had shown that metallic silver has no effect and since silver bromide can have no effect, experiments with these unknown, brominated products ought to confirm the sub-bromide theory to a certain extent. It appeared, however, that addition of these new substances had no more effect on a silver bromide emulsion than the metallic silver of the first series. A synthetic confirmation of the sub-bromide theory was not to be obtained in this way.

"One of the main arguments for the sub-bromide theory has always been the destruction of the latent image by bromine itself or, indirectly, by means of halogen carriers. Eder[1] recently cited this fact in his paper 'Silver Sub-bromide Theory versus Silver Germ Theory' as an argument in favor of the sub-bromide theory.

"A new method of treating the latent image on a silver bromide gelatine plate with bromide showed that, in this special case, the destruction of the latent image by bromine cannot be cited as an argument for the sub-bromide theory. Starting every time w th a freshly prepared, one percent, aqueous solution of bromine, I bathed one plate for five minutes before and another for five minutes after dipping in bromine water, and then washed the plates for two hours and a half in running water. The effect of bromine is the same before and after the exposure, there being no trace of an image on either plate, while the unwashed control plate gave an excellent negative. If other things are kept the same, and if the strength of bromine water is made 1.0 percent, the latent image is not destroyed completely, thus showing that the formation of a negative is not prevented by the previous treatment with this dilute bromine solution. In both cases there is still a trace of an image in the high lights, but even an

[1] Eder's Jahrbuch der Photographie, 14, 80 (1900).

exposure of twenty times the length does not give as much of an image as is obtained on the unbathed plate. In order to make the results more accurate, check plates were exposed, before being washed for two hours and a half, and after being so washed. Using these as standards it appeared that bromine had even more effect when added before the exposure than when added after it.

"The plates used in these experiments proved after fixing, to be strongly tanned and to be slightly reddish in color. Further investigations showed that the gelatine film, which had been treated with a one percent bromine solution, had become absolutely insoluble in boiling water. After the gelatine had been destroyed with concentrated nitric acid, the silver nitrate test showed that the gelatine had retained a recognizable amount of bromine chemically combined, a result which had practically been established before by Eder's investigations.[1]

"The fact that bromine affects the latent image more when added to the plate before the exposure than when added after it, seems at first sight to be a tremendous point against the sub-bromide theory. It ceases to have any weight now that it has been shown that bromine converts the film into an insoluble substance and remains in the gelatine to some extent even after prolonged washing of the plate. This reaction of the bromine is quite sufficient to explain the fact that less of an image is obtained when the bromine is added before exposure instead of after it.

"From these experiments it also follows that it is impossible to tell anything about the action of bromine on the latent image in the case of a dry plate because of the readiness with which the gelatine changes. For this reason I changed to collodion plates which I prepared according to the directions of Freiherr von Hübl.[2]

"When such plates are bathed in a one percent bromine solution not only is the latent image destroyed but the light-

[1] Eder's Handbuch der Photographie, 3, 68.
[2] Die Collodium-Emulsion, Halle (1894).

sensitiveness of the plate is decreased to such an extent that no image developed even after a normal exposure. When a 0.1 percent bromine solution was used, the latent image was destroyed completely, but an exposure after treatment showed that the plate retained about twenty-five percent of the light-sensitiveness of the original emulsion. This proves that bromine attacks the latent image more readily than the unexposed plate. On the other hand this experiment is not a proof of the sub-bromide theory because, as Eder[1] himself says, this experiment could even be made to harmonize with the silver germ theory.

"Both the one percent and the tenth percent bromine solution convert the negative obtained in the wet collodion process very quickly into silver bromide, which dissolves completely in sodium thiosulphate.[2]

"In any event the experiment on the action of bromine upon the latent image in a collodion film proves nothing against the subhalide theory. It seemed to me possible therefore that one might come out somewhere by the synthetic path, by adding sub-bromide to a silver bromide collodion emulsion. While no positive results had been obtained with a gelatine emulsion, there are so many differences between a gelatine and a collodion emulsion that it is not always safe to apply to one conclusions drawn from experiments with the other.

"I first prepared a grainless silver in collodion and from that a sub-bromide. It turned out that it is very difficult to reduce a silver bromide collodion emuls on in an alcoholic solution. If a developer and ammonia are added to the emulsion and the whole is poured into water the reduction is practically instantaneous; but I did not feel absolutely certain as to the fineness of the grain. I therefore reduced silver nitrate dissolved in collodion. To 10 g pyroxyline dissolved in 200

[1] Phot. Correspondenz, 36, 464 (1899).

[2] It was only after I had finished these experiments that I saw Eugen Englisch's paper, Ueber die Einwirkung von Brom auf das latente Bild. Arch. wiss. Phot., 1899, 282. His results in the main agree with mine.

cc alcohol + 200 cc ether were added 5 g silver nitrate dissolved in 5 cc water + 25 cc alcohol. I then added 1.5 g hydroquinone dissolved in 20 cc ether and next 5 cc ammonia (sp. gr. 0.910) diluted with 25 cc alcohol.

"The emulsion thus obtained is grainless like the silver gelatine emulsion and is dark brown in color. It was poured in a thin stream into water which was stirred vigorously. The precipitated lumps were washed for twenty-four hours in running water and were then rinsed a number of times for two hours in alcohol to remove the water. The lumps were dried superficially and dissolved at once in hot glacial acetic acid, since it did not seem safe to add bromine to an alcohol solution on account of the possible action of the bromine on the solvent. The solution of silver collodion in glacial acetic acid is reddish-brown. It was heated to 40° and a ten percent solution of bromine in glacial acetic acid was added slowly until there was one equivalent of bromine to two of silver. The silver collodion emulsion became at first bluish-green; next it changed to a dirty olive-green and finally to greenish-gray. After standing for ten minutes the emulsion was precipitated again by water, was freed from acid by washing for twenty-four hours was rinsed repeatedly in alcohol, and was dissolved again in an ether-alcohol mixture.

"Different amounts of this emulsion were added to a regular silver bromide collodion emulsion. The result was the one to be expected from the hypothetical silver sub-bromide. Development of a regular emulsion, to which a small amount of the sub-bromide emulsion had been added, resulted in a complete blackening of the plate. As a check a plate coated with the regular bromide emulsion was developed, and the sub-bromide emulsion was added to yet another plate which was then fixed in hyposulphite without having been developed. These experiments were duplicated, starting with a fresh batch of emulsions and I then decided to test the action on a silver bromide collodion emulsion of a silver emulsion which had not been converted into a sub-bromide emulsion. To my great surprise the same results were obtained with the silver

emulsion as with the sub-bromide emulsion. Consequently these experiments were more of an argument for the silver germ theory than for the sub-bromide theory.

"On account of the great theoretical importance of the matter, I tried to find some source of error in the experiments. Owing to the slow diffusion in the lumps of collodion, it was possible that, in spite of all precautions, some products had been formed which had a fogging action on silver bromide. It seemed simplest therefore not to purify the emulsion containing the reduced silver by precipitation with water but to pour it in a thin film on plates and afterwards to wash these in the usual way. The plates thus washed were dipped in alcohol and then the film was scraped off and dissolved in an ether-alcohol solution. Even then it was found that silver reduced by hydroquinone when added to a regular emulsion, caused the latter to blacken in the developer.

'In order to be certain that the fogging action was not due to decomposition products of the agent used to reduce the silver, I reduced silver nitrate dissolved in collodion by means of pyrogallol or of formaldehyde but the result was the same. I also tried ferrous sulphate. Since this salt is insoluble in alcohol, I bathed a collodion film containing silver nitrate in a thirty percent ferrous sulphate solution and thereupon washed at first in acidified water and then for a long time in pure running water. The water was removed from the film by means of alcohol and the film was dissolved in the ether-alcohol solution. The silver reduced by iron is whitish gray while that obtained with hydroquinone, pyrogallol or formaldehyde showed colors varying from greenish-brown to ruby-red. Since the silver obtained by reduction with ferrous sulphate has the same action on the silver bromide emulsion as the silver obtained by means of the organic reducing agents, there can be no question but that silver obtained in these ways acts just as it should act according to the silver germ theory. The action of the so-called sub-bromide emulsion does not prove anything for the sub-bromide theory

because it is always possible that there might have been some unchanged silver in the emulsion.

"The chief argument against the silver germ theory was that the latent image is not destroyed by nitric acid. In Eder's experiments he[1] used a silver bromide collodion plate containing an excess of silver nitrate. He laid stress on the fact that nitric acid was present in the film during the exposure. Eder drew the conclusion that very concentrated nitric acid does not destroy the latent image.

"It seemed to me that the presence of silver nitrate was undesirable, because in that case the results applied to one special case of the latent image. In order to test the action of nitric acid on a collodion emulsion, I started with a dilute acid (12.5 percent HNO_3). The plates were moistened with water, bathed for one minute in the acid, and then washed thoroughly. One plate was exposed before the treatment with nitric acid, one after treatment with acid, while a third plate was exposed and not treated with acid. The plate which was bathed in nitric acid before the exposure gave exactly the same image as the plate which was not dipped in acid at all. In the case of the plate dipped in acid after exposure to light, only the high lights and some of the half tones came out. The image was like the one that would be obtained by one-fourth the exposure.

"When an acid containing 33 percent HNO_3 is used, the plate which was exposed after the treatment with nitric acid gives the same results as the check plate. The one treated with the acid after the exposure gave only a slight precipitate in the high lights. Nitric acid of this concentration dissolves the fine-grained silver of a Lippmann photochrome rapidly but not the precipitate in a collodion process negative. It was necessary therefore to play the last trump and to use concentrated nitric acid (sp. gr. 1.4) containing 65 percent HNO_3.

"This acid attacks the collodion along the edges and the latent image disappears completely. The plate which was

[1] Eder: Phot. Correspondenz, 36, 276 (1899).

exposed after the treatment with acid gave nearly, though not quite, as strong an image as that on the check plate.

"We must therefore grant the possibility of destroying the latent image by nitric acid for the special case of silver bromide collodion emulsion not containing an excess of silver. Consequently the argument from nitric acid is not conclusive as to the silver germ theory. Of course we are moving in a vicious circle when we make use of assumptions in regard to the reactions of the hypothetical sub-bromide in order to prove the existence of such a substance. For instance it has long been considered as established that we have the reaction:

$$4Ag_2Br + 6HNO_3 = 4AgBr + 4AgNO_3 + N_2O_3 + 3H_2O.$$

If this reaction is correct, the action of nitric acid will not enable us to distinguish between the silver germ theory and subhalide theory. Since Otto Vogel has confirmed this reaction for his subhalide, we are fairly entitled to assume that any sub-bromide present in the latent image would be destroyed by nitric acid.

"We are therefore forced to draw the following conclusions:

1. Treatment with bromine does not help us to decide between the two theories because both metallic silver and sub-bromide are thereby converted into normal silver bromide.

2. Treatment with nitric acid proves nothing because the evidence points to the acid reacting both with metallic silver and with the sub-bromide. Since the latent image in a collodion emulsion is destroyed by nitric acid and since this was not the case in Eder's experiments with a wet plate and an excess of silver nitrate, we have an interesting illustration that the conception of a latent image is not necessarily the same for all processes.

3. The synthetic experiment of introducing silver or sub-bromide into the silver bromide emulsion brings out an important difference between gelatine and collodion plates in that both metal and sub-bromide change a collodion emul-

sion so that it can be reduced by a developer and do not have this effect on a gelatine emulsion.

"From these experiments can we deduce anything definite in favor of either of the two theories which we have been considering? So far as I can see, this is impossible. The fact that grainless si ver will cause the silver bromide in a collodion emulsion to be reduced by the developer is no proof that metallic silver is formed on exposure to light. While I recognize that I have overthrown one of the arguments against the silver germ theory, I do not believe that I have helped this theory by so doing.

"It does not seem to me quite justifiable to use as an argument for the silver germ theory the fact that a plate can be developed physically when fixed after exposure. Ever since the very beginnings of photography we have had instances of vapors or nascent solids condensing on solids at points which have been exposed to light; but it has not been necessary for us to postulate chemical reactions during the exposure to light. In 1842 Moser[1] gave a theory of the daguerreotype process in which he explained that no chemical process is involved but merely a condensation of mercury analogous to the condensation in his 'breath' pictures. He showed that a picture could be developed on a daguerreotype plate by means of water vapor. Under this heading we must include the interesting experiment by Waterhouse which was so much admired recently at the Paris Exposition. Waterhouse obtained an image by exposing a metallic plate of pure silver and developing with mercury. It is quite contrary to our ideas to assume a chemical change of the metal by the light.

"I wish to call attention also to the fact that the possibility of development after fixing would not prove anything for the germ theory even if silver germs were shown to be present, because we assume that the hypothetical sub-bromide is changed to metal and bromide by treatment with thiosulphate.

"Since we can accept neither the silver germ theory nor

[1] Pogg. Ann., 56, 177: 57, 1, 23 (1842); 58, 105; 59, 155 (1843).

the sub-bromide theory, it seems as though we ought to face the question whether there is reason to suppose that there is any reduction of silver bromide or any other chemical change of any sort as a result of the exposure to light. Of course there are several reasons which can be urged in favor of the assumption that a chemical change takes place. That bromine is set free from a bromide film as the result of a long exposure can easily be shown, even by the smell, if a dry plate is left for several hours in bright sunlight. That, however, proves nothing in regard to short exposures."

"The experiments on the action of nitric acid on silver bromide gelatine and on the latent image were undertaken to find out whether there was any metallic silver in the latent image. The experiments proved nothing in regard to this, because the gelatine was destroyed by the action of the concentrated acid necessary to dissolve the silver. Curiously enough other investigators do not seem to have noticed a secondary phenomenon which attracted my attention when I repeated the experiments.

"An exposed silver bromide gelatine plate, on which I had as usual left a broad unexposed strip, was placed for half a minute in a dilute nitric acid (8.3 percent). The gelatine was attacked but remained on the plate. The plate was washed thoroughly and was developed along with another from the same emulsion, which had received the same exposure but which had not been dipped in nitric acid. I obtained the entirely unexpected result that the plate which had been dipped in acid blackened even on the portions which had not been exposed, while the unexposed strip of the check plate remained quite clear. The same result was obtained even when the solution contained only one half to one fourth percent nitric acid and though no change in the gelatine was then visible. The effect disappeared when an extremely dilute nitric acid (0.05 percent) was used. A fogging of the unexposed silver bromide was also obtained by means of sulphuric acid but the sulphuric acid does not produce as marked changes in the gelatine as the nitric acid nor does it fog the plate so much. A

10 percent sulphuric acid is approximately equivalent to a 0.5 percent nitric acid. A 5 percent ammonium persulphate solution is about equivalent to these acids.

"That three substances which act so differently chemically should all act in the same way on silver bromide seems less intelligible than that the action should be upon the gelatine, though even this furnishes us with an interesting and difficult problem. We really know as little about development as about the latent image. Even when the gelatine, which forms a sheath, so to speak, round the silver bromide, is only slightly attacked, the bromide is nevertheless changed as though it had been exposed to light. This is even more remarkable than the fact to which I recently called attention, that substances which are not developers like gallic acid and formaldehyde are readily able to reduce silver bromide which has been precipitated with no protecting colloid present, quite regardless of whether there has been an exposure to light or not. We find it impossible to conceive that persulphate or a dilute acid should produce a chemical change in silver bromide; we have no reason to suppose that the silver bromide undergoes any physical change during the treatment; and consequently we must postulate a change in the gelatine. This last is the more probable because even a concentrated nitric acid seems to have no effect on silver bromide suspended in collodion.

"Instead of the formation of the latent image being a simple process, there seem to be several changes taking place simultaneously and the latent image seems to vary from one photographic process to another. We cannot say definitely that the formation of the latent image is due to a chemical change and it is also impossible to speak only of a physical change because the properties of the dispersing medium seem to have some chemical effect.

"It is possible that further experimental studies may enable us to formulate a real theory of the latent image. I think that I have proved that the ones under discussion are of no value."

"At the seventh general meeting of the German electrochemical society, Professor Richard Lorenz[1] of Zürich reported upon a series of experiments on the action of metals during the electrolysis of fused salts. Lorenz electrolyzed different fused halides. The halogen escaped and the metal regulus at certain temperatures dissolved to some extent in the melt. Lorenz says that 'it is not yet possible to say definitely whether this entirely general phenomenon is due: to the metal dissolving as such in the melt; to the formation of a lower halide; to the disintegration of the metal; or to several of these things combined.' So far we have considered it as an actual dissolving of the metal in the melt, because this has seemed to us the most plausible assumption. We will therefore use the term metal solution with the distinct proviso that this may be an inaccurate phrase. This solubility of the metals in the melt is connected with a chemical reaction which many halides undergo on melting, a reaction for which water is not necessary but in which light sometimes plays a part. This is a decomposition which is most marked with the iodides and which may be represented by the equation:

$$nMI_2 = [(n-1)MI_2 + M]\ [\text{Metal Solution}] + I_2.$$

"Even without the action of atmospheric oxygen or of moisture, traces of halogen escape and there remains a saturated solution of metal in the melt. Judging from this phenomenon, it seems not impossible that a similar reaction may perhaps play a part in the formation of the latent image on the photographic plate. It might be that, during the exposure, traces of bromine were set free as such from the silver bromide which gave rise to the formation of the first silver nucleus.'

"Although Lorenz does not tell us anything definite about the latent image, nevertheless it seems to me of great importance for our problem that the existence of such a solid solution of a metal in a halide has been established. It also seems to me not improbable that a metal in such a solid solution might behave differently towards chemical reagents

[1] Zeit. Elektrochemie, 7, 280 (1900).

than when present in the free state. This is another bit of evidence to the effect that it is not absolutely safe to reason from ordinary chemical reactions to processes taking place in a light-sensitive film. Granted that we were certain of the existence of a silver sub-bromide and that we knew the properties of this substance accurately, it would still not be permissible to assume that the latent image was the same as the sub-bromide because the two reacted in the same way with a given reagent. As a matter of fact we have no data as to the way in which silver sub-bromide is affected by the concentration of, or length of exposure to, nitric acid. From the widely discrepant results on the action of nitric acid on the latent image we are not justified in drawing conclusions either for or against the sub-bromide theory."

In a paper published later in the same year Lüppo-Cramer[1] says:

"It is quite unnecessary to make hypotheses in regard to the latent image because there is no reason to suppose that we have anything but silver bromide Silver bromide was precipitated from aqueous solution with an excess of bromide. It was spread out in a flat dish and exposed to diffused light for three hours, during which time it was kept moist with water and was stirred thoroughly so as to keep exposing a fresh surface. The silver bromide became grayish violet in color and bromine could be detected in water by the smell or by the reaction with silver nitrate. When the darkened silver bromide was heated with concentrated nitric acid, no silver was dissolved and the color did not change appreciably. The decomposition product of the silver bromide was not completely soluble in thiosulphate. Although most of it dissolved, the solution was turbid and grayish blue by transmitted light which indicated the presence of suspended silver. These reactions show that some bromine is set free during a long exposure to light.

"If we study carefully the action of light on precipitated

[1] Phot. Correspondenz, 38, 222 (1901).

silver bromide, we notice that there is a visible color change in a very short time. The silver bromide changes in a few seconds from the original greenish-yellow to a green which passes into a greenish-gray. When silver bromide has only changed to this extent, it dissolves completely in thiosulphate and no bromine can be detected in water. From this it appears to follow that a setting free of the bromine occurs only after a very long exposure, although light can cause in a very short time a change which can be recognized by the color passing through a series of shades."

"This indicates that when light acts for a short time, it merely changes silver bromide into a different, physical modification. It shows that a visible change in the color of the silver bromide is no proof that bromine has been set free. The marked color change produced by exposing silver bromide for three hours stands in no apparent relation to the infinitesimal amount of bromine actually set free. Consequently it is more reasonable to ascribe most of the difference in color to a molecular change rather than to credit it all to reduction.

" If we sum up our own results, we reach the following conclusions:

1. There is no proof of any chemical change in silver bromide as the result of a normal exposure, and there is no support for the silver germ hypothesis or for the sub-bromide hypothesis. The theory of sensitizers is unsatisfactory and not much can be said for any explanation of solarization involving the assumption of a sub-bromide produced by the action of light on silver bromide.

2. Since precipitated silver bromide can readily be reduced even when it has never been exposed to light, it is quite superfluous to postulate a chemically changed silver bromide in order to account for development.

3. Emulsified silver bromide appears to exist in a labile form (dissociated? ionized?) in which it reacts with many chemical substances (ripening and its prevention) in such a way as either to facilitate or check the action of light. Real reduction takes place only during development.

'We thus come back to the o'd view that normal exposure merely causes a change in molecular structure. This assumption is really the most rational if we keep in mind the simple fundamental fact that ordinary silver bromide, precipitated from aqueous solution and not exposed to light, is readily reduced even by such substances as gallic acid and aldehydes which are not really developers at all."

Although Lüppo-Cramer was not able to obtain a chemical development of a gelatine plate after adding silver nuclei this fact was demonstrated by Weisz[1] who showed that the important thing was to bring the silver particles in intimate contact with the silver bromide. He accomplished this by flowing the plate in a silver nitrate solution, letting it dry in the air, and dipping it for a moment first into a ferrous sulphate solution and then into a sulphuric acid solution. By regulating the concentration, any desired amount of silver could be precipitated. Satisfactory results were obtained with solutions containing 1–2 g $AgNO_3$ per 100 cc and 8–10 g $FeSO_4.7H_2O$ per 100 cc. It was also found that chemical development could be obtained when nuclei of gold, of platinum, or of silver sulphide were formed in the film in a similar manner. On the other hand no chemical development could be obtained when a solution of colloidal platinum was poured over the plate. The simplest explanation seems to be that the platinum did not diffuse into the gelatine.

While the experiments which have been quoted in this paper, are by no means conclusive as to the insufficiency of the sub-halide theory, they at least show that this theory has not as yet been able to account for all the facts. In the next paper of this series we shall discuss in detail the reasons for believing the latent image to be a solid solution.

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[1] Zeit. phys. Chem., 54, 323 (1906).

THE COMPOSITION OF SOLID PHASES IN FOUR-COMPONENT SYSTEMS

BY JAMES M. BELL

The composition of solid phases from which the mother liquid cannot be entirely removed and which are decomposed when washed with water or other liquid may be determined by the indirect method proposed by Schreinemakers[1] and later by Bancroft.[2] This indirect method is applicable to three-component systems, and consists in the use of triangular coördinates to represent the percentage composition of the mother liquid and of the "residue." By residue is meant the solid phase with the adhering mother liquid. It has been shown by Schreinemakers that when two ternary mixtures are themselves mixed, the composition of the resulting mixture lies on the line joining the points representing the original two mixtures. The converse of this is that if one of the original mixtures is known and the final mixture is known, the composition of the other original mixture lies on the line (produced) joining the two known points. This line is the "conjugate" line. Hence, the composition of a solid phase lies on the line produced joining the points: "liquid" and "residue." The intersection of two conjugate lines gives the composition of the solid phase. Or, if some other fact is established concerning the solid phase, such as the absence of one of the components, or the ratio in which two components are present, then only one conjugate line is sufficient to determine the composition of the solid phase. Thus the component absent from the solid phase has been called a "tell-tale," as it indicates how much liquid is present in the residue. Bancroft[3] has shown that this method is applicable to systems with any number of components, and has recalculated data of

[1] Zeit. phys. Chem., 11, 81 (1893).
[2] Jour. Phys. Chem., 6, 178 (1902).
[3] Ibid., 9, 558 (1905).

Morozewicz,[1] who studied the changes in melts containing the components: SiO_2, Al_2O_3, Fe_2O_3, FeO, CaO, MgO, K_2O, and Na_2O. It was shown that the ratio between all the components but Al_2O_3 was the same before and after partial crystallization took place. Hence all the components but Al_2O_3 remained in the melt and the solid phase was alumina. With another proportion of these same components it was shown that a spinel was separating from the melt. This tell-tale method has also been applied by Kenrick[2] in a study of the hydrates and acid salts of ferrous sulphate and by Cameron and Bell[3] in a study of the phosphates of calcium.

More recently the indirect method has been applied to four-component systems, the composition of the solution and of the residue being represented in an equilateral tetrahedron. The percentage composition may be represented, as the sum of the four perpendiculars on the sides of the tetrahedron from any point within the figure is constant, being equal to the height of the tetrahedron. The theorem also holds, that a mixture C of two other mixtures A and B lies on the line joining A and B. The usual difficulty of representing on paper a three dimensional figure presents itself. The usual method is by a perspective drawing which describes only the qualitative relations. A projection or several projections become necessary when quantitative relations are to be shown.

A graphic method of finding the composition of a solid phase in a four-component system by the use of two projections was described independently by Bell[4] in May 1907 and by Schreinemakers[5] in July 1907. In the first of these papers two triangles are used, the following data being plotted: (1) A, B, C+D and (2) A+B, C, D, where A, B, C and D represent the percentage composition of the corresponding

[1] Tschermak's min. petr. Mitt., [2] 18, 1 (1898).
[2] Jour. Phys. Chem., 12, 693 (1908).
[3] Jour. Am. Chem. Soc. 32, 869 (1910).
[4] Jour. Phys. Chem., 11, 394 (1907).
[5] Zeit. phys. Chem., 59, 641 (1907).

components. Thus in each triangle two of the coördinates give the composition of the material with respect to two of the components and the third coördinate gives the composition with respect to the sum of the third and fourth components. This method of representation is virtually a projection on a side of the tetrahedron by a line parallel to an edge of the tetrahedron. By finding the intersection of two or more conjugate lines the composition of the solid may be determined. In the paper by Schreinemakers just cited this same method has been described. In a later paper on the quaternary system: water-sodium chloride-barium chloride-copper chloride, Schreinemakers and deBaat[1] describe a similar method by the use of a tetrahedron, three of whose sides are equilateral right-angled triangles, the right angle representing water. Orthogonal projections are made on two of the right-angled triangles, and the composition of the solid phase may be determined directly from the intersection of the projected conjugate lines. This method is similar to the original method, being by two projections on two sides of the tetrahedron by lines parallel to an edge of the tetrahedron.

Besides these two methods of representation—oblique and orthogonal projections—Schreinemakers[2] mentions the possibility of the method of perspective projection. Here all points are projected on a side plane by lines from the opposite angle of the tetrahedron. I have not been able to find in the literature any further investigation of this method which, as we shall see, has certain advantages not possessed by the other method.

Suppose a point within an equilateral tetrahedron be projected on the side BCD by a line through the angle A. The points on the projecting line represent mixtures in which B, C and D are present in a certain definite proportion, the proportion of A being variable.

[1] Zeit. phys. Chem., 65, 586 (1909).
[2] Ibid., 65, 562 (1909).

Let the percentage composition of the mixture of the four components be *a* percent of A, *b* percent of B, *c* percent of C and *d* percent of D. Then the point in the side BCD to which the given point is projected will have the following coördinates:

$$\left(0, \frac{100\,b}{b+c+d}, \frac{100\,c}{b+c+d}, \frac{100\,d}{b+c+d}\right).$$

If these values be calculated for several solutions and the corresponding residues, the intersection of the conjugate lines in the plane BCD will give the point of projection of the solid phase. Thus the ratio B : C : D in the solid phase may be determined. By projecting the points representing solutions and residues, on another of the side planes of the tetrahedron by lines from the opposite angle, say B, the ratio A : C : D in the solid phase may be found. These ratios determine the composition of the solid phase. This method, however, requires calculation of the coördinates of the projected points, and also requires a calculation to find the composition of the solid. It is more complicated than by the method of parallel projection and consequently has not been used for the determination of a solid phase.

So far in this paper mention has been made only of the methods of determining the composition of one solid phase in contact with one liquid. By means of parallel projections Schreinemakers[1] has developed a method of determining a solid phase in contact with two liquid phases, when the solid phase consists of not more than three of the four components. Thus the method was applied to the system water-alcohol-ammonium sulphate-lithium sulphate at 30°, when there are two liquid layers and the solid phase contains no alcohol. In this case, three points are determined by experiment: the composition of each liquid layer, and that of the residue which contains both liquids. These three points fix a plane, at some point of which lies the composition of the solid phase. At the point of intersection of three such planes lies the com-

[1] Zeit. phys. Chem., 59, 641 (1907).

position of the solid phase. Where other relations are established, such as the absence of one or of two components from the solid, only two or one of these planes is necessary.

The following demonstration indicates what information may be obtained by the method of perspective projection. In the equilateral tetrahedron ABCD, let L_1L_3 be a boundary curve, *i. e.*, the curve of intersection of two surfaces, one representing solutions in equilibrium with solid I, and the other representing solutions in equilibrium with solid II. L_1L_3 therefore represents the solutions in equilibrium with two

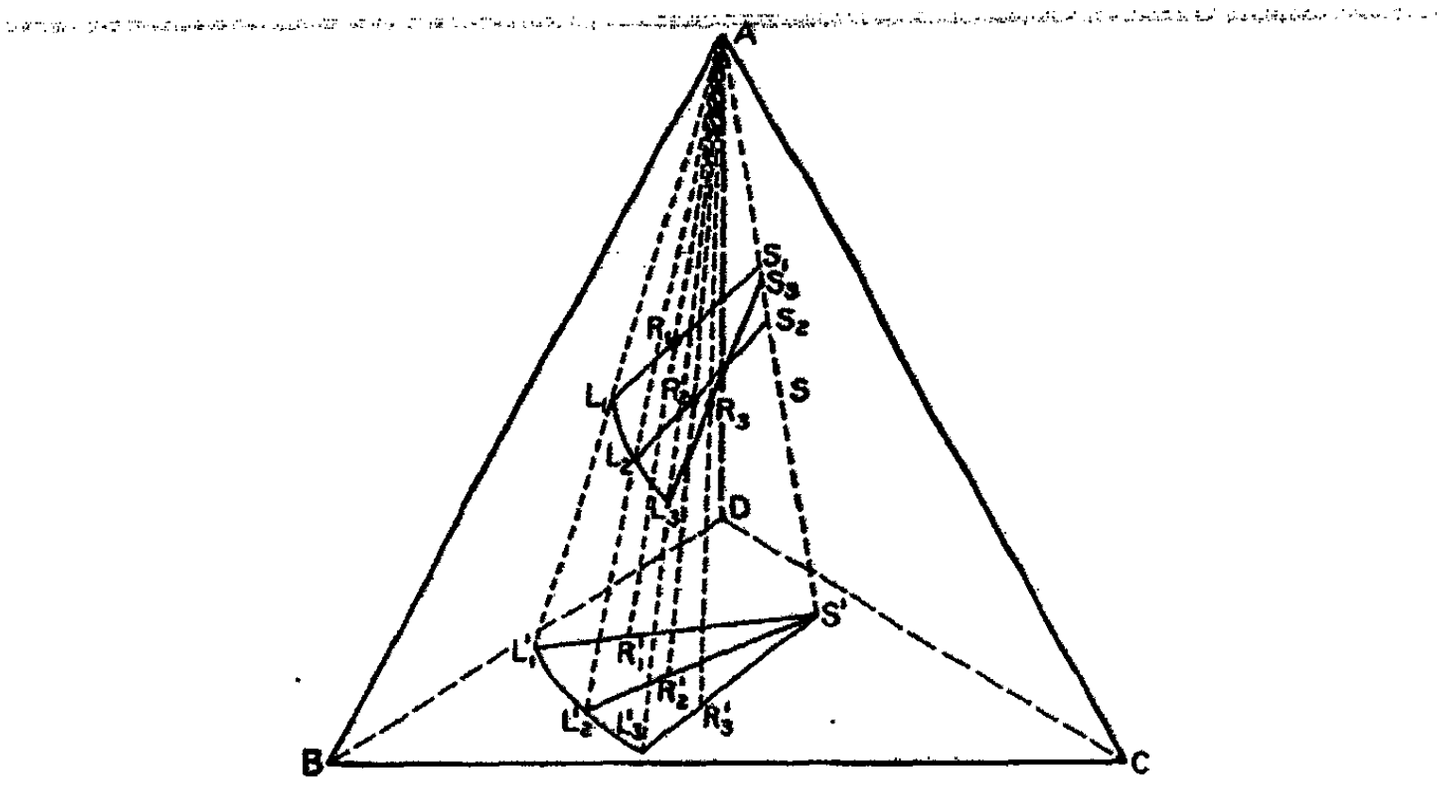

Fig. 1

solids and vapor at a given temperature. Suppose that the composition of one of the solids (I) is known, and is a simple salt, say A, and that the composition of the unknown solid is represented by S. The conjugate lines L_1R_1, L_2R_2 and L_3R_3 will cut the line AS, the point of intersection depending upon the relative quantities of A and S in the residue. Now as the line AS projects into the point S′, the projections of the conjugate lines $L'_1R'_1$, $L'_2R'_2$ and $L'_3R'_3$ will intersect in the point S′, the projection of S. Hence after finding experimentally the composition of several solutions and the corre-

sponding residues, the projections of these points are determined as above. The intersection of the projected conjugate lines fixes the position of S′, which gives us the ratio of B : C : D in the unknown solid phase.

In order to apply the method the following data by Schreinemakers and deBaat[1] on the four-component system H_2O–NaCl–$BaCl_2$–$CuCl_2$ at 25° are used. Table I contains the composition of solutions saturated with both NaCl and $BaCl_2.2H_2O$ and of the corresponding residues.

TABLE I

Solutions			Residues		
Percent NaCl	Percent $CuCl_2$	Percent $BaCl_2$	Percent NaCl	Percent $CuCl_2$	Percent $BaCl_2$
20.75	8.68	3.17	45.28	1.39	36.02
17.17	18.11	2.58	43.45	3.35	35.64
14.02	25.92	2.12	41.40	5.71	34.41

It is supposed that the composition of one solid phase is known, NaCl, and that the other is unknown. Table II contains the results of calculations, in which the sum: $BaCl_2$ + $CuCl_2$ + H_2O is considered as 100, and the percentage of each is found on that basis.

TABLE II

Solutions			Residues		
Percent $CuCl_2$	Percent $BaCl_2$	Percent H_2O	Percent $CuCl_2$	Percent $BaCl_2$	Percent H_2O
10.95	4.00	85.05	2.54	65.83	31.63
21.86	3.11	75.03	5.92	63.02	31.06
30.15	2.45	67.40	9.74	58.72	32.54

The accompanying diagram (Fig. 2) with the plot of these figures shows that the solid phase contains no $CuCl_2$

[1] Zeit. phys. Chem., 65, 586 (1909).

and that $BaCl_2$ and H_2O are in the proportion $BaCl_2 : 2H_2O$. Some other independent fact must be established to determine

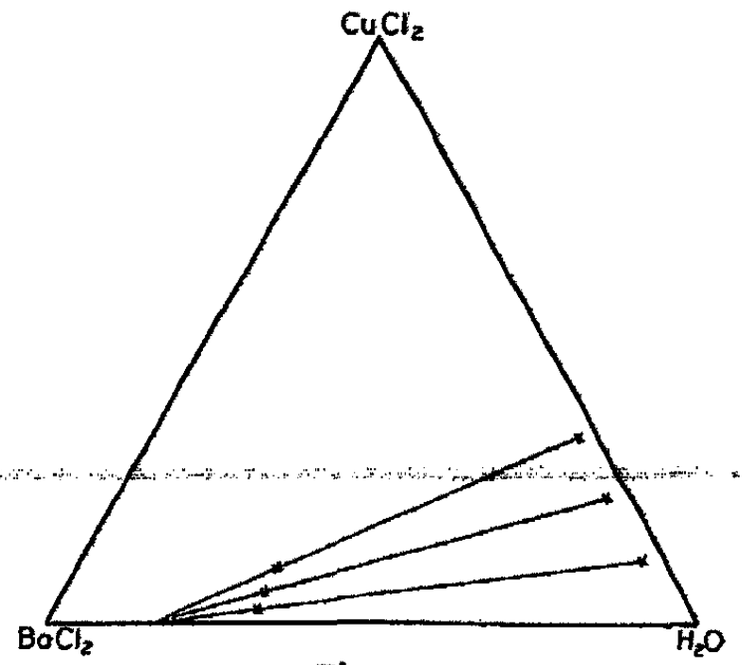

Fig. 2

how much NaCl is in the second phase. By this means the composition of the second solid phase is

$$n\text{NaCl}.\text{BaCl}_2.2\text{H}_2\text{O}$$

where n has to be determined by some other method. Similarly, if it is known that one of the solid phases is $BaCl_2.2H_2O$; the components are considered to be $BaCl_2.2H_2O$, NaCl, $CuCl_2$, H_2O, and the necessary calculations are made as before. The composition of the unknown solid will be

$$\text{NaCl}.m(\text{BaCl}_2.2\text{H}_2\text{O}).$$

Some further fact regarding the composition of the unknown solid phase is necessary in order to establish the value of m.

In this paper it has been shown that for four-component systems where two solid phases are present, one of which is of known composition, certain information may be gained regarding the composition of the second solid phase. If, A, the known solid be taken as one of the components of the system, the ratio in which the other three components exist in the unknown solid phase may be established. The method, however, does not indicate the amount of A in the unknown solid phase.

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THE ABSORPTION OF HYDROCARBON GASES BY NON-AQUEOUS LIQUIDS

BY ALONZO SIMPSON MCDANIEL

INTRODUCTION

In recent years our knowledge of the subject of solutions has been notably broadened by extensive investigations of solutions prepared with non-aqueous liquids.[1]

These researches, however, have largely been confined to the study of solids and liquids as "solutes" to the almost entire exclusion of gases. The primary object of the present investigation is to extend the work on non-aqueous solutions to include further studies of gases as "solutes."

This field of work has not received the attention which it deserves, partly perhaps because of the considerable experimental difficulties involved. These include the usual difficulties met in the manipulation of gases and in addition, those arising from the peculiar properties of non-aqueous as compared with aqueous solutions. Thus, for example, Gerhard Just states that, owing to the emulsifying action of many organic liquids upon mercury, no form of apparatus can be used for exact determinations in which the liquid is shaken up in contact with mercury as is done in the Bunsen absorptiometer; and likewise that the solvent action of such liquids on the lubricants commonly used on the stopcocks is a very serious difficulty which has to be dealt with. By far the most disturbing factor, however, is the preponderating influence of the very high and, in many cases, inaccurately determined or unknown vapor pressures of many non-aqueous liquids. This difficulty is further increased by the fact that the law of partial pressures (Dalton or Regnault) has not been definitely established for mixtures of gases and the saturated vapors of non-aqueous liquids. Consequently the

[1] See work of Kahlenberg and students: also, Franklin and Stafford, Sherry, Fitzgerald and others.

usual methods of calculation in the case of gases mixed with saturated vapors are not entirely satisfactory.

HISTORICAL

Determinations of the absorption of a number of gases by alcohol were made by Bunsen and his students. A limited number of additional non-aqueous liquids have been employed by a few other investigators.[1] The most extensive investigation in this field was carried out by Gerhard Just. He determined the absorption of H_2, N_2, and CO, in seventeen, and of CO_2 in forty-four organic liquids. Perhaps the most interesting result of his work was the observation that the absorption coefficient *increases* with temperature in the case of all gases that he investigated, except carbon dioxide, and with all absorbents except water and aniline. This interesting phenomenon received attention in the present work but the results do not confirm his observation.

The hydrocarbon gases were selected as suitable for an investigation of this kind because of (1) their relatively simple relationship to certain organic liquids that could be employed as absorbents; (2) their very great importance as constituents of illuminating and fuel gas; (3) the fact that very little is known about their absorption by non-aqueous absorbents.

The gases investigated, *viz.*, methane, ethane, and ethylene, were prepared by the method of Gladstone and Tribe. This consists in dropping an alcoholic solution of the required alkyl halide upon a zinc-copper couple. By this means the gas could be generated as needed, thus avoiding the necessity of storing and the consequent danger of contamination by the air. Details of the method used for each gas will be given in the description of the measurements made with the individual gases.

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[1] Skirrow: Zeit. phys. Chem., 41, 139 (1902); Levi: Gazz. chim. Ital., 31, II, 513 (1901); Woukouloff: Comptes rendus, 108, 674; 109, 61 (1889); Pagliana and Emo: Gazz. chim. Ital., 13, 278 (1883); Cniewosz and Walfisz: Zeit. phys. Chem., 1, 70 (1887); Ostrejko: Trudy. bak. old. imp. russk. teck. obtschtsch, 1886; Saussure: Bibliothéque britannique, 1812, 49–50; Just: Landolt-Börnstein Tables, Bibliography; Bohr: Amer. Phys., 1900.

THE APPARATUS

In designing the apparatus used in this work, the attempt was made to overcome as many of the difficulties already outlined as possible, especially those connected with the disturbing effect of the vapor pressure in the measurement of the temperature coefficients of absorption.

The essential parts of the apparatus are: (1) an ordinary gas burette (A, Fig. 1) and (2) an absorption pipette (B,

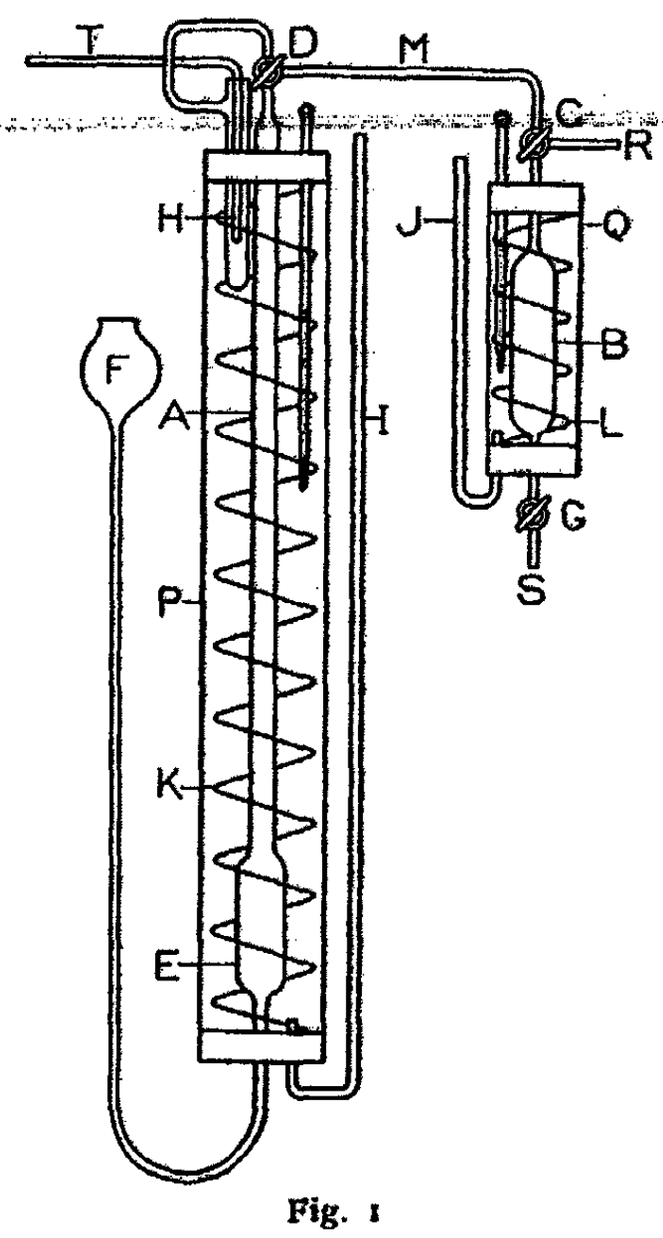

Fig. 1

Fig. 1) of the form first used by Ostwald. The burette and pipette are connected by means of a glass capillary (M) sealed directly onto each, so that the whole forms one solid piece of glass apparatus *without rubber or cement connections of any kind*; thus any possibility of leaks from these extremely

troublesome sources is entirely avoided. The whole apparatus is clamped solidly to a rigid support so that it can be taken up in the hands and shaken for the purpose of bringing the gas into intimate contact with the liquid. The pipette and burette are each provided with a three-way stopcock (C. D. Fig. 1). These can be turned in such a way as to allow the gas to sweep out the air from the connecting capillary. By the same means the two vessels may also be connected directly with each other as well as separately with the outside air or source of gas supply. The pipette and burette are each provided with a water jacket (P and Q). The temperature of each is regulated by means of the electrically heated coils (K and L) in a manner to be described later.

MANIPULATION

In carrying out a determination at room temperature, the procedure is as follows: The pipette is first completely filled with air-free absorbent. The method used to accomplish this important result will be described in a succeeding section. T is connected with the source of gas supply and the cocks C and D are turned in such a way as to allow the gas to sweep out the air from the capillary. The burette is then filled in the usual manner by lowering the leveling tube F, the cock D having been turned so as to connect T with E. Care is taken to keep the entering gas under a slight pressure by keeping the mercury level in F slightly above that in A. This prevents air from entering through any leaks in the train connecting the gas generator with the burette. The gas is completely saturated with the vapor of the absorbent in a manner to be described later.

After again allowing the current of gas to flow through the connecting capillary for a short time, the burette and pipette are connected with each other by turning the three-way cocks D and C in the proper direction. The determination of the amount of absorption is then made as follows: A portion of the gas is passed into the pipette by raising F and opening G, the displaced liquid being caught in a graduated

cylinder. The cock C is closed and the gas and liquid in the pipette brought into intimate contact with each other by shaking the whole apparatus. C is now opened to allow gas to enter from the burette to replace that absorbed. This process is repeated until, on opening C, there is no further decrease in the volume of gas in A. The volume absorbed is found by subtracting from the original volume of gas, the volume remaining in the burette plus the volume in the pipette. The volume of gas in the pipette is equal to the volume of the liquid drawn off. The volume of liquid remaining is easily calculated from the known volume of the pipette. The absorption coefficient or "solubility" is the ratio of the volume of gas absorbed measured at the temperature of the experiment to the volume of the saturated liquid. It may be reduced to the coefficient used by Bunsen, by dividing by $(1 + \alpha t)$.

In making measurements at higher temperatures than that of the room, the usual method has been to immerse the pipette in a thermostat kept at the higher temperature of the determination. The gas is measured in the burette at room temperature. A flexible capillary connection between the burette and pipette permits the latter to be shaken in order to thoroughly mix the gas and liquid. This method made it necessary in calculating the absorption coefficient to apply the usual correction for temperature and vapor pressure to the volume of gas in the burette. In the case of organic liquids with high vapor pressures the corrected volumes, when the temperature difference is 10° or more, may be 2 or 3 times as great as the volume actually measured, so that the errors of observation are correspondingly multiplied. Moreover, in many instances the vapor pressure of the absorbing liquid is but inaccurately determined or unknown so that one is limited in the choice of absorbents. In such cases, G. Just calculated the vapor pressure by means of the formula of Ramsay and Shields, but such a method, of course, leads only to approximate values. These errors are likewise magnified in the calculation. Another source of error which

applies to any method in which the observed volumes are corrected for vapor pressure, lies in the fact that the vapor pressure of the liquid may be altered by the "solution" in it of certain gases; since the law of Dalton (or Regnault) has not been tested for saturated vapors of non-aqueous liquids in presence of certain gases. This factor is likely to become appreciable, more especially in those cases where the "solution" of the gas in the liquid is comparable, in kind as well as degree, with ordinary solutions.

The method employed in the present research sought to eliminate these errors arising from the effect of the vapor pressure of the absorbent, *by keeping the burette and pipette at the same temperature.* When this is done the *partial pressure of the gas in the burette is equal to that of the gas in the pipette; hence no correction of the volume of gas in the burette is necessary.*

Two general methods of accomplishing this result suggested themselves: First, the whole apparatus could be immersed in a thermostat; or secondly, the burette and pipette could be heated in separate thermostats. The second method was chosen for the reason that it seemed to present fewer difficulties, especially with the arrangement which was finally adopted. This consisted in heating the water in the burette and pipette jackets (P and Q, Fig. 1) by means of electrically heated coils of manganin wire. These coils (K and L, Fig. 1) were connected in series. The rate of evolution of heat in the jackets was adjusted in the first place, by varying the length of the manganin wire, until the temperature was the same in each jacket. Only one adjustment was necessary, since the ratio of the rates at which heat is liberated in the jackets remains the same whatever the strength of the current. Consequently the temperature of the two jackets may be increased or decreased an equal amount by simply increasing or decreasing the current strength. Starting with both jackets at the same temperature, when the current was increased, the temperature rose more rapidly in the jacket with the greater radiating surface, but both finally came to

equilibrium at the same temperature. Slight variations in the temperature of the room produced no greater fluctuations in the temperature of the jackets at higher than at lower temperatures. Stirring was accomplished by blowing air through the tubes (I and J Fig. 1). The effectiveness of this method of stirring was surprising; no difference in temperature could be detected between the top and bottom of the long column of water in the burette jacket. This was due in large part to the fact that the water was heated very uniformly by the coil of wire, so that there was never any great difference in temperature between any two portions of the column, even without stirring. The necessary connections of wire and flexible rubber tubing did not interfere with shaking the apparatus. By this method of heating, the pipette and burette could easily be kept at the same temperature, the difference never exceeding 0.1° C. (A thermometer was kept in each jacket at all times.)

The electrical connections were arranged so that the water in either the burette or pipette jacket could be heated separately. This arrangement made it possible to heat each thermostat to the desired temperature very rapidly by employing a heavy current for a short time. When both had been heated to the same temperature in this manner, the coils were connected in series and the current adjusted at the proper strength to keep the temperatures at a value as near the chosen temperature as possible. It usually required about 20 minutes for the temperatures to reach a condition of equilibrium, the final temperature in the two jackets usually being slightly above or below that to which they were originally heated. The measurement of the absorption could then be made exactly as at ordinary temperatures.

The same samples of gas and liquid could be used for determining the absorption at a series of succeeding higher temperatures. After completing a determination at one temperature the stopcock was closed so as to shut off the burette from the pipette. The water in the burette jacket was then heated to the temperature of the next determination.

Before connecting the pipette and burette by opening the cock D, the amount of expansion caused by the increase in temperature was carefully noted, a series of readings being taken at temperatures a few tenths of a degree apart in order to be certain of obtaining the value corresponding to the final temperature of equilibrium (see above). The cock D was now opened and the pipette heated to the temperature of the determination, both burette and pipette being held at the same temperature in the manner described above. In calculating the absorption at the higher temperature, correction for this *observed* expansion of the gas and saturated vapor was applied to the original volume taken (see equation 4 below). *Thus the whole series of determinations depended in no way upon a knowledge of the vapor pressure of the solvent, nor likewise upon any assumption regarding the validity of the law of partial pressures for mixtures of a gas and the saturated vapors of non-aqueous liquids.* On the other hand, the value of the vapor pressure at each temperature used may be calculated from the data obtained, if the value for any one temperature be assumed.

The coefficient of absorption was calculated from the measurements obtained, by means of the formula,

$$A_1 = \frac{V^\circ_{b_1} - V_{b_1} - V_{p_1}}{V_{L_1}} \qquad (1)$$

where A_1 represents the coefficient of absorption or "solubility;" $V^\circ_{b_1}$ the total volume of gas taken, *measured at the temperature t_1 of the first determination*; V_{b_1} the volume of gas remaining in the burette at the end of the determination at t_1; V_{p_1} the volume of gas in the pipette measured at the temperature t_1, and V_{L_1} the volume of liquid in the pipette measured at the temperature t_1. For the absorption coefficient at the temperature t_2 the formula becomes

$$A_2 = \frac{V^\circ_{b_2} - V_{b_2} - V_{p_2}}{V_{L_2}} \qquad (2)$$

where the separate expressions have the same significance as in formula (1) except that the volumes represented are

measured at the temperature t_2 of the second determination. For example, $V^\circ_{b_2}$ is the total volume of gas taken, *measured at the temperature t_2 of the second determination.* The formulas used in calculating the absorption coefficients at the succeeding higher temperatures, t_3, t_4, etc., are entirely similar to (1) and (2).

In formula (1) the separate expressions (or terms) on the right of the equality sign are *observed* volumes obtained by direct measurement (except V_{L_1} which is equal to the *total* volume of the pipette minus V_{p_1}). This arises from the fact that the first determination is always made at the same temperature (t_1) at which the original volume of gas is measured. When this is not the case, as, for example, in the determination at the next higher temperature t_2, the values of the expressions in the right hand member of the equation are obtained indirectly from the direct measurements. This is done in the case of formula (2), for example, by means of the following equations:

$$V^\circ_{b_2} = V^\circ_{b_1} + V^\circ_{b_1} \frac{V'_{b_2} - V_{b_1}}{V_{b_1}} \qquad (3)$$

where V'_{b_2} is the volume of gas in the burette at the beginning of the determination at t_2 before the pipette and burette are connected by opening the cock D. The expression rep-

$$\frac{V'_{b_2} - V_{b_1}}{V_{b_1}} \qquad (4)$$

resents the *coefficient of expansion* (at t_2) of the mixture of gas and saturated vapor for the unit of temperature ($t_2 - t_1$).

$$V_{L_2} = \frac{V_{L_1}}{1 + at_1 + bt^2_1},$$

where the expression ($at_1 + bt^2_1$) represents the coefficient of expansion at 0° C of the liquid concerned.

$$V_{p_2} = V_p - V_{L_2} \qquad (5)$$

where V_p is the total volume of the pipette.

By substitution in equation (2), the complete formula

for calculating the absorption at temperature t_2 therefore becomes

$$A_2 = \frac{V^\circ_{b_1} + V^\circ_{b_1}\frac{V'_{b_2} - V_{b_1}}{V_{b_1}} - V_{b_2} - V_p + \frac{V_{L_1}}{1 + at_1 + bt^2_1}(1 + at_2 + bt^2_2)}{\frac{V_{L_1}}{1 + at_1 + bt^2_1}(1 + at_2 + bt^2_2)}. \quad (6)$$

In like manner the formula for the temperature t_3 becomes.

$$A_3 = \frac{V^\circ_{b_2} + \frac{V'_{b_3} - V_{b_2}}{V_{b_2}} V^\circ_{b_2} - V_{b_3} - V_p + V_{L_3}}{V_{L_3}}. \quad (7)$$

By substituting the value of

$$V_{L_3} = \frac{V_{L_1}}{1 + at_1 + bt^2_1}(1 + at_3 + bt^2_3) \quad (8)$$

the final formula becomes

$$A_3 = \frac{V^\circ_{b_2} + \frac{V'_{b_3} - V_{b_2}}{V_{b_2}} V^\circ_{b_2} - V_{b_3} V_p + \frac{V_{L_1}}{1 + at_1 + bt^2_1}(1 + at_3 + bt^2_3)}{\frac{V_{L_1}}{1 + at_1 + bt^2_1}(1 + at_3 + bt^2_3)}. \quad (9)$$

Saturating Gas with the Vapor of the Absorbent

In dealing with non-aqueous liquids this part of the determination is of much more importance than when working with aqueous absorbents. This is in part due to the higher vapor pressure of most organic liquids and in part to the fact that in dealing with absorbents water is present in every part of the apparatus thus offering most favorable conditions for complete saturation of the gas even before it is collected in the burette. Very early in the present investigation, it became evident that the usual method of merely bubbling the gas through the liquid does not effect complete saturation especially when dealing with liquids of relatively high vapor pressures; equilibrium is not reached in the short time allowed for contact. It has been found necessary before taking each reading, to bring the liquid and gas into very intimate contact and to allow ample time for the establishment of equilibrium; *the mere presence of the liquid phase does not insure complete saturation.*

In some cases the error in volume due to incomplete saturation may amount to as much as 20 percent of the total volume of gas absorbed. The very great importance of making certain that the liquid is completely saturated with the gas is thus evident.

Two different methods for saturating the liquid with the gas were used in the present investigation. In the one most frequently used, a few drops of the liquid were introduced into the burette before drawing in the gas, a small pipette being employed for this purpose. Just sufficient liquid was added to form a second meniscus above that of the mercury. Before reading off the volume of gas in the burette, the apparatus was allowed to stand until equilibrium was established. This usually required only a short time since rapid diffusion was aided by the film of liquid on the sides of the burette. This was formed by the layer of liquid on top of the mercury as the gas was being drawn into the burette. If this film was subsequently destroyed by evaporation (when the burette was heated to a higher temperature), it was again formed by holding the apparatus in a horizontal position and gently shaking so as to bring the liquid in contact with the entire inner surface of the wall of the burette. No emulsifying action upon the mercury was noticeable in any case, even in carrying out a regular determination when it was necessary to thoroughly agitate the contents of the pipette. This was due in part to the small amount of liquid present in the burette, and in part to the fact that the slight shaking of the whole apparatus that was necessary for the thorough mixing of the liquid and gas in the pipette, scarcely disturbed the liquid in the burette owing to the much smaller diameter of the latter. By another method, the gas was first supersaturated by allowing it to bubble through some of the solvent kept at a higher temperature than that at which the determination was to be made. It was then brought down to saturation by allowing it to bubble slowly through some of the liquid contained in the tube H (Fig. 1) which was immersed in the water of the burette jacket. Condensation

in the connecting capillary tubes was prevented by keeping them at a higher temperature by means of a coil of wire wound about them, through which an electric current was passed. Short pieces of platinum wire wedged into the capillary openings through the plugs of the stopcocks, aided in preventing condensation at these points by conducting heat across these less heated portions of the capillary opening. This method, however, could be used only with liquids whose boiling points were sufficiently constant, *i. e.*, liquids that could be completely distilled without a variation in the temperature of the vapor greater than 0.1° C. for, in sweeping the air from the capillary by means of a current of the gas the more volatile constituents of the liquid are drawn off first with the result that the gas that is finally led into the burette is bubbled through a liquid of lower vapor pressure.

Removing Air from Absorbent

In most of the work on the absorption of gases, great care has been taken to completely remove "dissolved air" from the absorbing liquid and this step has been considered perhaps the most important part of the determination; but no one seems to have pointed out just what influence the presence of air in the liquid may have upon the measurements obtained. The results of the present work indicate that the effect of dissolved air is to decrease the absorption at higher temperatures to a greater extent than at lower temperatures. This is evidenced by the fact that in several instances when no effort was made to completely expel the air from the liquid, the absorption coefficient *decreased* with increase in temperature, whereas the opposite was the case when the air was expelled from the liquid. Similar results were obtained when the method of Just was employed. In this method the air is removed by boiling the liquid in an elongated flask under diminished pressure using a reflux condenser. It is allowed to cool while the air pump continues in operation. The flask is then detached from the condenser and only the lower layer transferred to the pipette by means of a tube,

one end of which is immersed in the liquid the other being attached to the lower outlet of the pipette. The liquid is then drawn up into the pipette by applying suction to the upper opening. When extreme care was exercised, this method seemed to give satisfactory results, but it was very difficult by its use to obtain duplicate measurements with

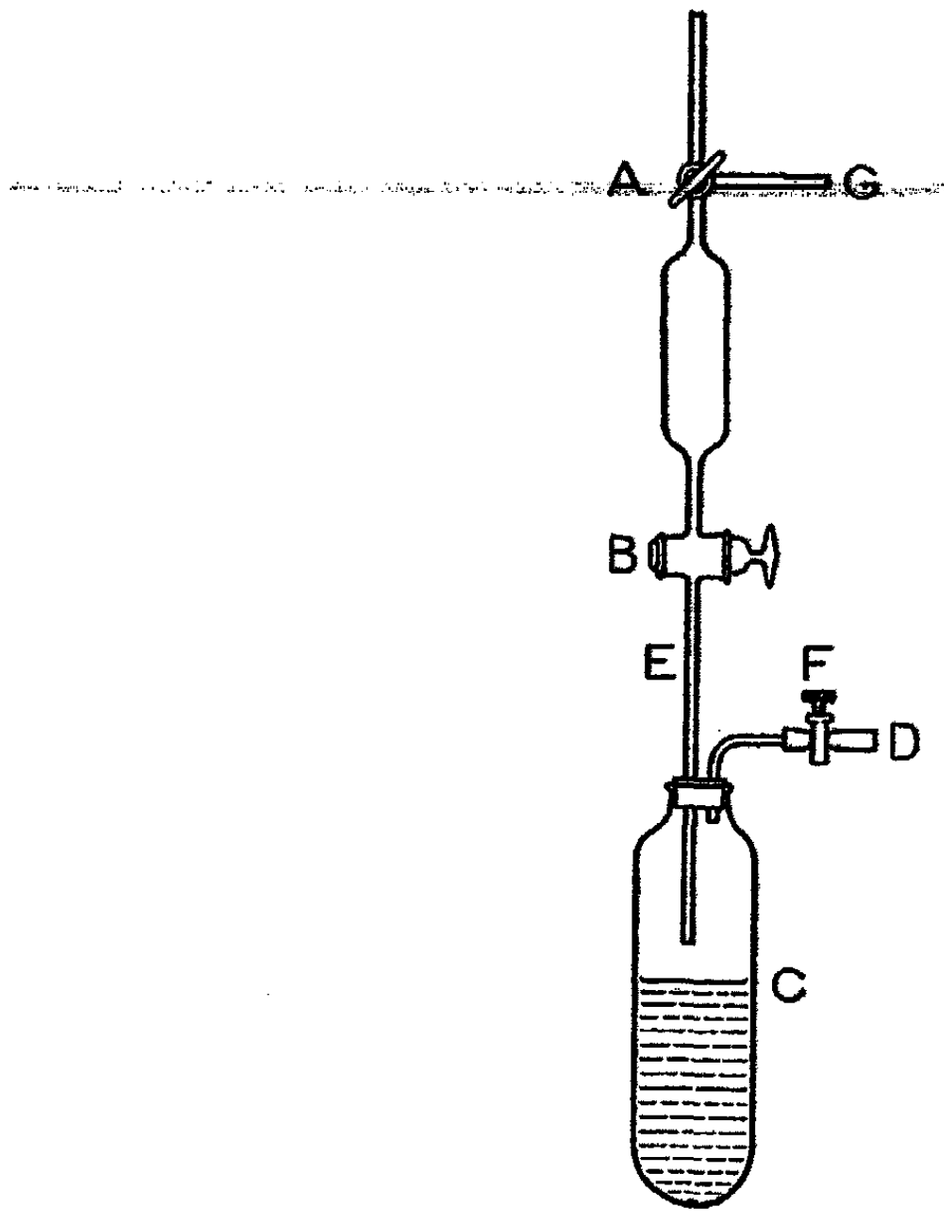

Fig. 2

the same gas. This was attributed to the absorption of air during the short time that the liquid was in contact with the atmosphere while it was being transferred to the pipette. The method employed by Levi is not open to this objection but cannot be used with liquids whose vapors are capable of dissolving the lubricant from the stopcocks. In this con-

nection it is of interest to note that Levi repeated Just's determination of the absorption coefficient of nitrogen in methyl alcohol and found that the absorption decreased with increase in temperature whereas the opposite was observed by Just. In the present work, the attempt was made to overcome the above-mentioned difficulties in the following manner: The liquid was boiled under diminished pressure in the flask C (Fig. 2) attached directly to the lower opening of the pipette by means of the rubber stopper as shown in the figure. Connection with the air pump is made at D. During the boiling the lower opening of the inlet tube E is above the surface of the liquid in C, the stopcock B being closed. When the air has been completely expelled, the screw pinchcock F is closed while the air pump is still in operation. The flask C is now raised until the lower end of E reaches nearly to the bottom of the flask. The air pump is now connected at G and the cock A opened so as to make connection with the pipette. B is now opened and the inflow of air through D regulated by gradually opening F in such a manner that the liquid is very slowly forced up into the pipette. In this manner the liquid never comes into contact with the air under full atmospheric pressure but only under greatly diminished pressure. The absorption of air under these conditions can only be inappreciable, especially since the liquid in the flask remains perfectly quiet, and only the lower portion is used.

METHANE

It was found advantageous to modify the gas generating apparatus described by Gladstone and Trib [1] by using tap funnels with very much longer stems so that the liquids could be made to flow in against the pressure of the gas in the apparatus. By this means the rate of evolution of the gas could be controlled by regulating the amount of methyl iodide solution added from the tap funnel; also it enabled one to keep the zinc-copper in the "scrubber" always moist

[1] Jour. Chem. Soc., 45, 154 (1884).

with alcohol thus preventing the escape of methyl iodide vapors with the gas. The alcohol vapors were absorbed by allowing the gas to pass first through a U-tube containing a little water and then through two U-tubes each charged with glass beads and concentrated sulphuric acid.

The gas was generated as needed and between determinations the gas left in the apparatus was kept under pressure to avoid any possible contamination with air. After each determination and before setting the generator aside until again needed, the methyl iodide in the tap funnel and stem was replaced with alcohol, care being taken that no air bubbles were allowed to enter at the same time. Thus the generator was always free from air and ready for immediate use. In this manner one charging with zinc-copper sufficed for several determinations. Since no unused methyl iodide was left in the apparatus there was no danger of the formation of iodine and hydriodic acid by the prolonged action of light which would result in the contamination of the methane with hydrogen. A combustion analysis of the methane gas generated in this manner gave the following results:

	cc
Vol. of gas taken	28.4
Vol. of oxygen taken	60.4
Vol. remaining after combustion	32.1
Vol. remaining after absorption with KOH	3.6
Vol. of CO_2 formed	28.5

The absorption measurements with methane are tabulated in Table I.

Under A_{25} are tabulated the absorption coefficients of the various liquids calculated from the observed absorption at the temperature nearest 25° by use of the value of $\frac{dA}{dt}$ for that temperature.

TABLE I

Absorbent	Temp.	Absorption Coeff., A	$\frac{dA}{dt}$	Bunsen's Coeff., B	A_{25}
Methyl alcohol (99 percent)	22.1°	0.4436		0.4102	0.4431
			—0.00019		
Methyl alcohol (99 percent)	30.2	0.4278		0.3883	
			—0.00034		
Methyl alcohol (99 percent)	40.0	0.3938		0.3436	
			—0.00126		
Methyl alcohol (99 percent)	49.8	0.2695		0.2278	
Ethyl alcohol (99.8 percent)	22.2	0.4628		0.4282	0.4581
			—0.00158		
Ethyl alcohol (99.8 percent)	30.1	0.4503		0.4051	
			—0.00182		
Ethyl alcohol (99.8 percent)	40.0	0.4323		0.3771	
Isopropyl alcohol	21.5	0.4620		0.4275	0.4584
			—0.00104		
Isopropyl alcohol	29.9	0.4532		0.4081	
			—0.00132		
Isopropyl alcohol	40.0	0.4400		0.3837	
			—0.00077		
Isopropyl alcohol	60.3	0.4244		0.3478	
Amyl alcohol	22.0	0.4532		0.4196	0.4500
			—0.00108		
Amyl alcohol	30.1	0.4444		0.4002	
Benzene	22.1	0.4954		0.4600	0.4844
			—0.00367		
Benzene	35.0	0.4484		0.3976	
			—0.00560		
Benzene	40.1	0.4198		0.3661	
			—0.00564		
Benzene	49.9	0.3645		0.3081	
Toluene	25.0	0.4852		0.4450	0.4852
			—0.00150		
Toluene	30.0	0.4778		0.4300	
			—0.00101		
Toluene	40.1	0.4675		0.4080	
			—0.00120		
Toluene	50.2	0.4545		0.4013	
			—0.00043		
Toluene	60.0	0.4502		0.3690	

TABLE I (*Continued*)

Absorbent	Temp.	Absorption Coeff., A	$\frac{dA}{dt}$	Bunsen's Coeff., B	A_{25}
Xylene (meta)	21.1°	0.5146		0.4778	0.5096
			—0.00125		
Xylene (meta)	30.5	0.5028		0.4529	
			—0.00028		
Xylene (meta)	50.0	0.4972		0.4203	
			—0.00102		
Xylene (meta)	60.0	0.4870		0.3992	
Hexane	22.2	0.6035		0.5585	0.5918
			—0.00397		
Hexane	40.2	0.5320		0.4639	
			—0.00147		
Hexane	49.7	0.5180		0.4380	
			—0.00209		
Hexane	60.0	0.4964		0.4068	
Heptane	22.2	0.7242		0.6720	0.7116
			—0.00426		
Heptane	30.1	0.6906		0.6221	
			—0.00234		
Heptane	40.0	0.6675		0.5820	
Pinene (b. p. 155–160°)	20.0	0.4888		0.4565	0.4623
			—0.00265		
Pinene (b. p. 155–160°)	30.1	0.4620		0.4163	
			—0.00165		
Pinene (b. p. 155–160°)	39.1	0.4472		0.3914	
			—0.00055		
Pinene (b. p. 155–160°)	45.0	0.4440		0.3811	
			—0.00732		
Pinene (b. p. 155–160°)	55.2	0.3694		0.3076	

Ethane

This gas was prepared from ethyl iodide and zinc-copper in an apparatus entirely similar to that used for the preparation of methane. The reaction proceeds more slowly so that the generating flask must be warmed by immersion in a water bath kept at a temperature of approximately 40° C. A combustion analysis of a 30 cc sample showed that the gas contained no measurable amounts of impurities capable of detection by this method.

TABLE II

Absorbent	Temp.	Absorption Coeff., A	$\frac{dA}{dt}$	Bunsen's Coeff., B	A_{25}
Methyl alcohol (99 percent)	22.5°	2.0235		1.8710	1.9769
			—0.01866		
Methyl alcohol (99 percent)	30.1	1.8817		1.6952	
			—0.01002		
Methyl alcohol (99 percent)	45.2	1.7304		1.4852	
Ethyl alcohol (99.8 percent)	22.0	2.3344		2.1616	2.2897
			—0.01492		
Ethyl alcohol (99.8 percent)	30.0	2.2151		1.9951	
			—0.01494		
Ethyl alcohol (99.8 percent)	40.0	2.0657		1.8020	
			—0.02144		
Ethyl alcohol (99.8 percent)	50.0	1.8513		1.5651	
Hexane	22.1	3.3508		3.1035	3.2878
			—0.02111		
Hexane	30.0	3.1842		2.8680	
			—0.02022		
Hexane	55.0	2.8812		2.4008	
Heptane	25.0	4.5000		4.1220	4.5000
			—0.01600		
Heptane	30.0	4.4200		3.9820	
			—0.01568		
Heptane	40.0	4.2632		3.7182	
Ethyl acetate	22.0	3.0800		2.8521	3.0725
			—0.0025		
Ethyl acetate	30.0	3.0601		2.7575	
			—0.0059		
Ethyl acetate	40.0	3.0003		2.6178	
Amyl acetate	22.0	3.5761		3.3085	3.5059
			—0.0234		
Amyl acetate	30.0	3.3891		3.0518	
			—0.0249		
Amyl acetate	50.0	2.8909		2.4433	

Ethylene

This gas was prepared from rectified ethylene dibromide and the zinc-copper couple in exactly the same manner as in the case of methane and ethane. The reaction is very vigorous so that an ice-bath is necessary to control the rate of evolution of the gas. A combustion analysis was not made. This

was not considered necessary since the gas was completely absorbed by bromine water.

The results of the absorption measurements are recorded in Table III.

TABLE III

Absorbent	Temp.	Absorption Coeff., A	$\frac{dA}{dt}$	Bunsen's Coeff., B	A_{25}
Benzene	22.0	3.0100		2.7865	2.9281
			—0.0273		
Benzene	35.0	2.6545		2.3530	
			—0.0115		
Benzene	50.0	2.4820		2.1000	
Hexane	22.0	3.0382		2.8141	2.9896
			—0.0162		
Hexane	35.0	2.8265		2.5050	
			—0.0242		
Hexane	45.0	2.5863		2.2190	
Heptane	22.4	3.4630		3.2071	3.4061
			—0.0219		
Heptane	35.0	3.1860		2.8245	
			—0.0190		
Heptane	39.0	3.1100		2.7215	
Acetone	20.0	2.5709		2.2900	2.4834
			—0.0175		
Acetone	35.0	2.3084		2.0460	
Limonene	22.0	no constant equilibrium; increased from 2.753 to 3.05+ in 12 hours under diminished pressure.			

Discussion of the Measurements

The temperature of 25° has been selected as the most suitable one at which to make comparisons of the various absorption coefficients, principally because the values at this temperature are the least subject to error on account of the lesser influence of the vapor pressure at the lower temperatures. It is evident, however, that such an arbitrarily chosen temperature does not offer the best basis for comparison. Nevertheless, it is probably true that if it were possible to make comparisons at temperatures representing "corresponding states" of the liquids the relations between chemical con-

stitution and absorptive power of the absorbents would become more evident than at an arbitrarily chosen temperature. Consequently any such regularities which manifest themselves at any particular temperature chosen for convenience sake would probably persist or even become more clearly defined if the measurements were made under the more ideal conditions mentioned. It is not necessary to assume that the relationship would necessarily remain the same in character, but the *regularity* might become more evident although of a somewhat different nature.

In this connection it should be noted that the values of $\frac{dA}{dt}$ vary greatly for the same liquid in many instances so that predictions as to solubility at other than the observed temperatures are unsafe. Moreover, the errors of observation in determining the value of this coefficient are probably very considerable.

For the foregoing reasons, a comparison of the absorption coefficients of the different liquids at the arbitrarily chosen temperature of 25° does not seem unwarranted.

In Table IV, the liquids are arranged in the order of their increasing absorptive power at 25° for the different gases. Those marked with an asterisk (*) were used with more than the one gas.

It is seen that the *general* order of the liquids common to two or more gases is the same in each column; or in other words the *relative* absorptive powers of the liquids are *generally* the same for all gases *of this group*.

The same generalization was noted by Just for the gases which he investigated. From this he sought to draw the general conclusion that the absorptive power of a given liquid is a characteristic constant of that liquid and may be related to certain other specific constants of the same liquid, as, for example, its index of refraction. Winkler likewise endeavored to establish a relation between the absorptive power of water and its viscosity.

TABLE IV

Methane	Ethane	Ethylene
*Methyl alcohol	*Methyl alcohol	Acetone
Amyl alcohol	*Ethyl alcohol	*Benzene
*Ethyl alcohol	Ethyl acetate	*Hexane
Isopropyl alcohol	*Hexane	*Heptane
Pinene	Amyl acetate	
*Benzene	*Heptane	
Toluene		
Xylene		
*Hexane		
*Heptane		

TABLE V

N_2	CO	H_2	CO_2
Benzene	Benzene	Amyl alcohol	Amyl alcohol
Xylene	Amyl alcohol	Benzene	Xylene
Amyl alcohol	Xylene	Acetone	Toluene
Toluene	Toluene	Amyl acetate	Benzene
Methyl alcohol	Ethyl alcohol	Xylene	Ethyl alcohol
Ethyl alcohol	Methyl alcohol	Ethyl acetate	Methyl alcohol
Acetone	Amyl acetate	Toluene	Amyl acetate
Amyl acetate	Acetone	Ethyl alcohol	Acetone
Ethyl acetate	Ethyl acetate	Methyl alcohol	

A comparison of the absorptive powers of the above liquids for the group of hydrocarbon gases investigated, with the absorptive power of the same liquids for the group of gases investigated by Just, shows, however, that the relations are quite different for the two *groups* of gases. Table V shows the relative order of the liquids as determined by Just for N_2, CO, H_2, and CO_2 respectively. It is particularly noticeable that the absorptive power of the alcohols as compared with the hydrocarbon liquids is exactly reversed. In other words, *the specific nature of the gas may exercise quite as much influence as the nature of the liquid.* The regularities respecting the relative absorptive powers of the liquids then are due to similarities among the gases themselves.

When the chemical relations of the gases to the group

of liquids is such that no "specific action" is probable, the similarities or dissimilarities in their *physical* properties may play a greater rôle than their purely chemical properties (*i. e.*, their relationship to other substances upon which they have some "specific action"). Thus in the group of gases investigated by Just the members are quite dissimilar in their chemical properties, yet this investigator has pointed out that what regularities there are in their "solubilities" in various organic liquids are closely related to the physical properties of the gases—notably their critical constants and molecular weights.

When these physical properties are nearly the same for any two or more gases, as for example in the case of CO and N_2, the difference between their absorption coefficients for a given liquid is relatively small, and their *ratio* is practically constant for all the liquids investigated.

These same generalizations apply to a lesser extent to the case where "specific action" of the gases upon the liquids is probable but where the gases are chemically similar to each other. The cases investigated in the present work fall in this category, but the specific influence of the nature of the liquid exercises a much greater influence in this case and the constancy of the *ratio* for any two gases holds only for liquids that are chemically similar, *e. g.*, for homologues. These observations are illustrated to some extent in Table VI but the available data are hardly sufficient to warrant the deduction of any general conclusion.

With a given gas, the absorption coefficients of homologous liquids vary in a rational manner. Thus with methane the absorption increases regularly with the molecular weights of all homologous liquids except the alcohols, and with these it first increases and then decreases. With the other gases the absorption increases with the molecular weights of all homologous liquids investigated.

The influence of the specific nature of both liquid and gas are strongly emphasized by the results obtained with limonene with both ethane and ethylene. There is evidence

that in these instance slow chemical combination takes place. These cases require further investigation.

TABLE VI

	$\frac{CH_4}{C_2H_6}$	$\frac{CH_4}{C_3H_4}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{CO}{N_2}$
Methyl alcohol	2.241	—	—	1.38
Ethyl alcohol	2.002	—	—	1.33
Benzene	—	1.653	—	1.47
Hexane	1.800	1.980	0.9088	1.47
Heptane	1.580	2.088	0.7536	1.47

A comparison of the solubilities of hydrogen and methane in some of the liquids used with the latter gas suggests the possibility of separating these gases by taking advantage of their differences in solubility in these liquids. For this purpose a liquid of very low vapor pressure whose vapors could be subsequently removed without great difficulty would be most desirable. For these reasons pinene seems the most suitable since its vapors could be removed by strong HCl solution. An attempt was made to analyze a mixture of H_2 and CH_4 by this means but unexpected difficulties arose and the time available did not permit of a thorough test of the method.

The Temperature Coefficient

In the earlier preliminary measurements with the apparatus described in this paper, before the importance of insuring complete saturation of the gas with the vapor of the liquid was fully realized and before the method of freeing the liquid from dissolved air was developed, a *positive* temperature coefficient was observed in many instances. Later determinations, in which these sources of error were avoided as much as possible, showed these results to be incorrect. From the tables it is seen that $\frac{dA}{dt}$ is *negative in all the cases investigated in the present work.* In this connection the results obtained by Levi[1] for the absorption of nitrogen by

[1] Loc. cit.

methyl alcohol are of the greatest importance. He found that by taking the greatest precautions to free the liquid from dissolved air the absorption *decreased* with *increase* of temperature whereas Just had observed the exactly opposite behavior.

Summary

1. The absorption of methane in ten, of ethane in seven, and of ethylene in five different organic liquids has been determined at a series of temperatures lying between 20° and 60°.

2. A new method of temperature control for keeping pipette and burette at the same temperature has been devised which enables *direct* observations of the absorption to be made at the different temperatures, thus eliminating many of the errors arising from the effect of the vapor pressure.

4. Certain relations between the absorptive power and chemical constitution of the liquids have been pointed out.

In conclusion the writer wishes to express his sincere appreciation of the helpful suggestions and friendly advice of Professor Kahlenberg during the progress of this work.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, April, 1911

NEW BOOKS

The Principles of Scientific Management. *By Frederick Winslow Taylor. 16 × 24 cm; 144 pp. New York: Harper and Brothers, 1911. Price: $1.50 net.*—Everybody will agree that a green man will do less work than a man who has had practice at the job. Mr. Taylor goes much farther than this. He shows that the maximum output can be obtained only after somebody has made a careful quantitative study of the particular kind of work, keeping in mind the elimination of unnecessary movements and the necessity of resting at specified intervals. By doing this, Mr. Taylor increased the amount of pig iron which could be loaded on a car by one man in one day, from 12.5 tons to 47 tons. The number of bricks laid per hour was increased from 120 to 350. The head work necessary to bring about these improvements must be done by the management because the laborer has neither the time nor brains to make such experiments.

If the laborer is to maintain these high efficiencies, he must be paid more, and Mr. Taylor finds that an increase of sixty to one hundred percent over the normal wages will give the best results.

While this work of Mr. Taylor's is extraordinarily interesting, people might ask what it had to do with chemistry and why a book of this sort should be reviewed in a chemical periodical. There are many answers to such a question. In the first place, Mr. Taylor has shown the practical value of research work, which is the very point that the chemist is always making. The value of a chemist to a company depends very largely on his ability to do research work.

When the chemist becomes works' manager, he has not only his own problems to look after, but it becomes essential for him to work out the applications to his own factory of the principles laid down by Mr. Taylor.

There is still another side of the problem which bears directly on the research work of the chemist and which, therefore, affects the technical man and the university man alike. What is the efficiency of our own research work? Are our experiments so planned that we are getting the maximum in the way of conclusions from each experiment? Do we always ask ourselves what we are going to prove by a given experiment, whether it is the best experiment for the purpose, what we have proved by it, and why we did not get the results that we expected? So far as the reviewer can judge, the question of efficiency is of secondary importance in most university laboratories. If results are obtained, that is enough. We are so thankful to get results that we do not bother our heads much over the question whether the results could have been obtained more quickly and with less expenditure of energy. Of course, this is all wrong; but it does happen, and a book, like this one by Mr. Taylor, is of great value in calling our attention to the probable magnitude of our inefficiency. It is impossible to say that this book will help every chemist but it will certainly help many.

Wilder D. Bancroft

A Text-Book of Organic Chemistry. *By William A. Noyes. Second edition, revised. 13 × 19 cm; pp. xvii + 537. New York: Henry Holt and Company, 1910. Price: $1.50 net.*—The German translation of the first edition

was reviewed about two years ago (13, 157), and now we have the second English edition. The author states in the preface that, "in this edition the chapter on compounds of interest in physiology and pathology has been rewritten on the basis of the classification of proteins recently adopted by the American Society of Biological Chemists and the American Physiological Society."

Wilder D. Bancroft

Organic Chemistry for the Laboratory. *By W. A. Noyes. 16 × 24 cm; pp. xi + 291. Easton, Pa.: The Chemical Publishing Co., 1911. Price: $2.00.*—"In preparing a second edition of this book, chapters on the Analysis of Organic Compounds, on General Operations, on Ethers, on Hydroxy and Ketonic Acids and on Carbohydrates have been added, and thirty new preparations have been included. The chapters in the book have also been rearranged to correspond more nearly with the order used in the author's text-book. It is hoped that this rearrangement will not interfere with the use of the book by those who prefer some other text-book as the basis for their instruction.

"The tables for nitrogen have been recalculated on the basis of modern values for the weight of one liter and for the coefficient of expansion of nitrogen. Some similar tables in common use are about 0.4 percent in error because old, erroneous values for these constants were used in their preparation."

Like all other laboratory manuals in organic chemistry this one is a survival from the time when physical chemistry was not taken seriously. The student is not expected to ask questions. It is his duty to do the experiments as set down and to get the specified yields; but nothing more.

Wilder D. Bancroft

The Theory of Ionization of Gases by Collision. *By John S. Townsend. 13 × 20 cm: vii + 88 pp. New York: D. Van Nostrand Company, 1910. Price:* $1.25.—In the preface, the author says:

"After studying the changes which take place in the conductivity of gases through which ions are passing under various conditions, I was led to propose the theory of ionization of collision to explain the development of currents in gases. The accuracy of the theory has been established by a number of experiments specially arranged to measure conductivities which could be compared with the values obtained from theoretical considerations. The researches have brought to light the fact that ionization by collision takes place when comparatively small potential differences are established between electrodes in a gas at a suitable pressure, so that considerable multiplication of the ions may be obtained by this process with forty or fifty volts, and consequently with comparatively small velocities of the ions.

"This is in marked contrast with the previously known cases of ionization produced by the motion of ions through a gas, where the velocity is always very high, sometimes approaching that of light. Such, for instance, is the case for the negative particles emitted by radio-active substances, or for the particles composing the cathode rays and the Lenard rays when the ions move with velocities that are acquired under the action of some thousands of volts."

Wilder D. Bancroft

ON THE LAWS OF ENERGY AND THE PHYSICAL SIGNIFICANCE OF ENTROPY

BY M. M. GARVER

Professor Planck, in his excellent treatise on thermodynamics,[1] claims that the second law of thermodynamics can be completely expressed only in terms of the entropy function; and he is undoubtedly correct in his assertion in so far as any known "law" is concerned, because the entropy function evidently includes the remaining necessary fundamental facts not included in the first law. As yet no simple and, at the same time, sufficient expression of the second law of thermodynamics has been found that does not require frequent reference to the entropy function as the final test of legitimacy. The mathematical reader will recognize in this procedure the part played by the fundamental differential equation in so many physical investigations. We may know some fundamental fact that *must* be recognized, some condition that *must* be fulfilled; to suppose the contrary is absurd. Now if we can express this requirement in the form of a mathematical equation—oftentimes only in the differential form—then any conclusion that we arrive at must, when expressed mathematically, satisfy the fundamental equation of condition. It cannot otherwise by any possibility be a correct solution of the proposed problem. It will be unnecessary to offer illustrative examples; suffice to say that generally the fundamental fact is known and expressed in the form of a differential equation; but in the case of the second law of thermodynamics, we know without doubt the differential, or integral, equation that must be satisfied, but we do not know any simple physical expression for the law, or laws, which that equation represents. That it does represent some physical law or laws is evident from the results that have been obtained from its use and that have been con-

[1] Translated by Ogg, p. 98.

firmed in so many ways. The equation itself is not open to serious question; but what does it mean, or represent physically?

As may be gathered from the preceding remarks I have no special quarrel with the entropy function; its validity and utility are too well established for me to take exceptions to it further than to suggest that it may possibly be made more general in its applications if we can succeed in expressing it in terms of simple laws of energy which shall be axiomatic in form and command assent from the mind as soon as the terms in which the laws are expressed, are comprehended.

In the first place, the form of the entropy function should suggest that its substance cannot be expressed in one simple law because it is a function of two independent variables; and its complexity and difficulty of comprehension and expression in words therefore arise from the fact that now one, then another and different law, takes precedence in producing the observed effects. This peculiarity will be all the more puzzling if it is supposed that but one law is the source of the observed phenomena, or that it is derivable from a single natural law; for in that case the law will sometimes appear to hold and in other instances fail to account fully for the observed results. If, on the other hand, we assume the entropy function to express two entirely different and independent laws we should expect to find just what is observed—an infinite shading in the effects depending upon the relative interaction of the two laws. By independent and different laws, I mean natural actions that cannot be derived from each other by reasoning, or be deduced from each other without some postulate more fundamental than any with which we are at present acquainted.

In the present paper it is proposed to consider more particularly only those general energy relations which may be illustrated by reference to chemical and physical processes; the thermodynamics of mechanical processes being omitted as lying without the scope of the present discussion.

On the assumption that we are dealing with independent

natural laws not deducible from each other, probably the most satisfactory way will be to state the proposed laws according to which it is supposed the natural actions take place and then by analysis of the phenomena test whether they become explicable in terms of the proposed laws. It should be emphasized at the outset that while any proposed forms of the laws must be simple and easily comprehensible, they must necessarily be abstract and general in form if they are to include and explain all the infinite variety of natural phenomena. It can be only by the use of terms of the widest generality that widely different and diverse phenomena can be included.

First Law.—The law of conservation. The total energy of an isolated system can be neither increased nor diminished by any interaction among its parts if the various forms of energy not already existing as heat are measured by their ability to produce heat. In other words: The heat value of the energy of an isolated system is constant.

Second Law.—The law of redistribution. In an isolated energy system all spontaneous actions between the different parts of the system are due to a non-uniform distribution of the contained energy and take place in such a manner as to diminish the inequalities of distribution of the energy of the system.

Third Law.—The law of transformation. All transformations of energy from one form or type into another take place during the equalizing transfers arising from a non-uniform distribution of energy and take place in such manner as to aid in diminishing the inequalities of the distribution of the energy undergoing transfer.

A careful examination of the proposed laws will show that they contain nothing more than a formal statement of facts that have for a long time been assumed to be true—assumed without actual recognition, perhaps, that they do constitute the fundamental facts and *all the necessary facts* of the underlying natural laws. An expression of a natural law cannot, in the nature of the case, contain details; but it

cannot be a correct statement of a law of Nature if any well authenticated exception to it is shown to exist. All that the writer claims in the statement of the laws is that the facts generally assumed to be true and made use of as they happen to be required, necessitate *three* formal statements instead of two,—that the law of transformation is entirely independent of the law of transference (or redistribution). This is shown by the fact that frequently transfer takes place without transformation; but transformations are always the result of, or are accompanied by, transfers. The writer can see no logical necessity in this relation of these two facts. They are simply facts of Nature. If so, they should be recognized as such formally, especially if such formal recognition aids us in comprehending the processes involved. To summarize concisely we may say that in general, in a fluid system: (*a*) Interchanges in all directions are universal. (*b*) With non-uniform distributions, more energy is transferred in some one direction than in others. (*c*) Under favorable conditions transformations take place. (*d*) Transformations are some function of the rate of transfer. (*e*) As an ideal limiting case all the energy transferred may be transformed.

Of course, such statements which claim to represent natural actions are not in the ordinary sense axiomatic. They are merely generalized statements assuming that to be true which we may prove to be true in as many instances as we care to test, or in the nature of the case, can test experimentally. If an exception can be shown and established, the generality is disproved and such statement ceases to be a law or to represent a law of Nature.

If anyone doubts that the proposed laws express natural actions let him deny them and defend the negative. He will probably find that their rejection leads to greater mental difficulties than their acceptance. It is only in this sense that Newton's laws are axiomatic. Anyone is privileged to reject them; but he finds himself in greater difficulties by denying their validity than by accepting them.

It will be evident on examination that the above state-

ments are more general than the postulates denying the possibility of perpetual motors of the first and second kinds frequently assumed as the basis of thermodynamic theory, but are not inconsistent with them. From the first law we may deduce that

No heat engine can by any means be made to supply continuously more heat than is supplied to it, or any engine more energy of any kind than is dynamically equivalent to the energy supplied to it.

From the third law it is evident that

No engine of any kind can by any means be made to maintain continuously, or restore and maintain when changed, the state of the system which initially set it in motion; and the difference in the energy state which initially established the motion will disappear the more quickly the greater the activity of the engine.

It is quite evident also, that the statements as to the conditions limiting engine operations are not co-extensive with the statements of the laws themselves. Other and additional conclusions quite as important in a philosophical sense may be drawn from the conceptions included in the statements of the laws. A number of such conclusions consistent with and deducible from the laws were given in a former paper;[1] to deduce them from the "engine law" in the absence of the general laws would be impossible. The first two laws, it is evident, are entirely distinct and assert two distinctly different facts; but neither of them touches on the peculiar fact that engages most of our attention in our study of the dynamics of Nature—namely, transformations. Hence a third law is necessary to include all the fundamental facts observed and made use of in our study of the energy turmoil. A short study of the second and third laws will show why they are generally included as one, but will also show why such attempt to include two distinct kinds of facts in one statement leads to confusion: First one aspect, then the other,

[1] Jour. Phys. Chem., 15, 20 (1911).

engages the attention without a distinct recognition that we are dealing with two distinct sets of facts. It is true that all transformations presuppose and imply transfers, but on the other hand all transfers do not imply corresponding transformations. A condition favorable to transfers is a prerequisite to transformations which may, or may not, take place. I see no way of deducing the third law from the others that would not involve an assumption uniting all three in one —and such assumption would be metaphysical rather than physical.

As to the significance and application of the third law let us consider a mixture of oxygen and hydrogen gases in "false equilibrium." There is an apparently uniform distribution of the matter and motion. If we introduce a hot glass rod, below a certain limiting temperature, a pure transfer, or redistribution, of the energy introduced by the rod, takes place without producing any appreciable transformation. But suppose that an electric spark introduces at one point in the system an excessively high rate of motion. The action that now takes place is such as to equalize the differences in distribution and during the redistribution transformations take place, heat is produced and distributed, work may be done; and the production of the work when it appears during the process aids in the reduction of the resulting contained motion. The same sort of process as the latter may be traced in the case of an explosion of nitro-glycerine. At some point in the system, by the action of external agency a point of high activity is introduced by forcing a rearrangement of the molecules, or atoms, at that point. The result is an entire rearrangement and redistribution of the contained matter and motion of the system. The last two cases are chosen because one represents "composition" and the other "decomposition" and rearrangement. Again, suppose a quantity of a volatile liquid be introduced into a vacuous space much larger than the volume of the liquid. The substance will occupy the whole space open to it, in two phases if the liquid is sufficient in quantity, or in one, if the space is large enough.

The process by which this is accomplished consists of *both transfer and transformation*, the transformation—the work of disgregation—aiding in diminishing the motion causing the transfer by which the whole average motion is lowered, as shown by a fall in temperature. The disgregation work—the separation of the molecules against their gravitating attraction—is work of exactly the same nature, in my judgment, as the lifting of a weight against the attraction of the earth, the difference consisting merely of being "internal" instead of "external"—molecular instead of molar. It should be particularly noted that the process by which the space is occupied is a transference of energy accompanied by a transformation. The total energy transferred is not measured by the kinetic energy in the vapor since a part was transformed into "internal work;" this internal work, however, is available for ready retransformation back into the kinetic energy of heat when the volume is reduced to the original volume of the liquid by the action of external agency. In the supposed instance, since there has been no heat enter or leave the substance, according to the usual definition, which omits reference to reversibility, there should be no increase in the entropy of the substance during such a process. But there has been increase of entropy, nevertheless, because there has been a transfer of energy without available work or energy sufficient to restore the original state. If the change in volume and fall in temperature had taken place in consequence of external work performed this work might have been available to restore the original temperature and volume. If just sufficient for the purpose, the entropy change would be zero; but the internal work is sufficient only to restore the original temperature when the volume is decreased by external agency. The work required to restore the substance to its original volume keeping the temperature constant is then a measure of the change in entropy due to the pure transfer of energy by which the space was occupied. This peculiarity will be found to hold also for the expansion of a perfect gas into a vacuum which process represents a pure

transfer without transformation. We shall find that the entropy function is one that in an isolated system increases for all transference of energy and decreases with all transformations into potential forms. When these are equal, being opposite in sign, the change is zero. This aspect of the entropy function will be considered again later.

Since all statements by means of which we endeavor to express our conceptions of the order of Nature should consist of simple affirmations without the introduction of hypothetical causes of the observed or assumed actions, all reference to the intensity of the contained energy was avoided in the enunciation of the second and third laws. But the idea of intensity of energy as the "cause" of transfer will be convenient oftentimes, in order to avoid circumlocution; and besides this fact it may be necessary in order to determine the degree of the inequality of distribution to measure the quantity corresponding to the intensity of the energy when we wish to know the relation of transfer to our measure of the intensity. Also in our study of energy forms it will be necessary in consequence of their multiplicity of characteristics to indicate what we mean by "kinds" and "types" of energy. It is generally agreed that there are but two kinds of energy—kinetic and potential—and that *all* spontaneous transfers of energy are kinetic, although the matter in motion may carry with it a potential form or forms to be later transformed into the energy of motion, or heat. It is in consequence of this mode of transfer that the actual kinetic transfer accompanied by transport of material is no real measure of the total energy transferred. It is this peculiarity that constitutes a marked characteristic during change in phase and that enables us by Landsberger's method, to boil a solution at a higher temperature than is possessed by the entering vapor of the pure solvent.

In the former paper[1] the terms "type" and "intensity" were used rather loosely as convenient terms rather than as

[1] Loc. cit.

terms possessing scientific accuracy although it was mentioned that the actual energy per unit volume was not a definite criterion as to the direction an energy transfer would take unless considered as applying to a single type. Hence it is important to determine, if possible, just what constitutes a "type of energy" before the term intensity can be applied advantageously and used consistently. Whether we succeed in attaching scientific accuracy to the proposed terms or not the necessity and desirability for such definitions are easily shown by reference to a well-established experimental fact. When a solution and a pure solvent are contiguous and in thermal communication the volume of the solution increases at the expense of that of the pure solvent. It is also shown that the direction of transfer of the vapor may be changed by warming the solution. Now in the first instance it is evident that in consequence of the heat of vaporization heat must pass in a direction opposite to the direction of transfer of the vapor. It is easy to see that the heat returned is merely the heat of vaporization; the total energy of the solution increasing as that of the solvent diminishes. Energy is, then, undergoing transfer from the solvent to the solution; and just as we speak of water flowing spontaneously from higher to lower levels, or of heat passing spontaneously from the hotter to the colder body, so we may say that energy of some form, or type, is passing spontaneously from a higher to a lower intensity. It is a fair scientific question, to endeavor to determine and classify the nature of the type and the character of the intensity, which is thus forced on the attention of the scientific observer. Professor Planck seems to be satisfied with the statement that the process being irreversible takes place because the entropy is thereby increased. It is plainly evident that since no work is done when the two liquids are at the same level, that the entropy of the system as a whole is increasing. The transfer of the heat alone proves that much; but the total entropy increase must exceed that due to the heat transfer to the same extent that the energy transfer exceeds the heat transfer. We have here, then, a

case in which the entropy of a body (the solution) increases spontaneously while giving out heat. Now to my mind, the term "entropy function" is a name used to designate a certain special energy function; and an entropy change is not "explained" until it is expressed in terms of energy changes. Since we are interested more particularly in chemical and physical processes let us consider in more detail the conditions determining a transfer of energy in and between fluids.

We may assume from the kinetic theory that the internal kinetic energy of a fluid may be represented by $\Sigma(\frac{1}{2} n m u^2)$ where n is the number of molecules per cc, m the mass of the molecule and u^2 the mean square of the molecular velocities of translation. It is evident that when the m's are all of the same species, the transfer of energy will depend upon the n's and u's, the transfer taking place so as to equalize the differences. The n's and the u's may be changed by pressure and temperature changes which are entirely independent of each other and may take place in such manner as to compensate each other with regard to equilibrium. This statement still holds when the m's are of different species *provided* the two species of molecules are separated by an *impervious* flexible diaphragm by means of which *a change of density is* prevented. It is customary to regard the changes in pressure and temperature by which the n's and u's are changed, as energy changes, while the changes in the m's by which the density is changed, although recognized, in a way, as giving rise to measurable energy effects, are yet regarded as something different from, or more than, mere energy changes—a change in the material. However, from the law of Avogadro for gases we have $n_1 = n_2$ for equal temperatures and pressures; and from Maxwell's law $\Sigma(\frac{1}{2} m_1 u_1^2) = \Sigma(\frac{1}{2} m_2 u_2^2)$ where the subscripts represent different gases. It follows, therefore, on the average for different gases at the same temperature and pressure that

$$\frac{u_1^2}{u_2^2} = \frac{m_2}{m_1}$$

which is supposed to hold throughout a considerable range of temperature. The u's are regarded solely as energy criteria but the m's are not always so regarded because they cannot, in general, be equilibrated by temperature and pressure differences alone; but they do determine the direction of transfer of energy, nevertheless, just as definitely (although in a different manner) as a difference in the other variables. It seems to me that both simplicity and generality are to be gained by regarding the m's as pure energy factors, because they are frequently the fundamental factors in determining the direction of transfer of energy during a chemical or physical reaction or process. This is already done in all the general theorems relating to chemical processes but an exception is made in the cases of diffusion and dilution. The general theory should be broad enough to include them also. By the law of distribution of energy a process will continue until *all* the factors which affect equilibrium are equally (on the average, by the statistical law of averages) distributed throughout the free space open to them except as modified by the presence and formation of solid and liquid phases in which each phase has its own peculiar and independent uniformity. The m's are no exception to this law; differences in the m's give rise to differences in the velocities of the moving elements of exchange; hence a change in the m's has an effect on energy interchanges analogous, inversely, to a temperature change. Each separate species in each phase tends to uniform distribution in the phase; and equilibrium is not reached until the vector sum of the energy passing *through* any arbitrarily chosen plane area is equal to zero. This criterion of equilibrium will be found to be independent of phase, or is unaffected by the presence of phases. Kinetic equilibrium is reached only when each species of molecule, or type of kinetic energy represented in each fluid phase, is uniform throughout the phase and when the interchanges between two phases are equal and opposite in direction. This statement as to uniformity does not, of course, apply to interchanges through selective walls and to the membranes found in the cell-walls

of living organisms. In the absence of such boundaries, however, the process of redistribution of the contained matter and motion after a disturbance in the equilibrium of an isolated system may take place with explosive violence in consequence of a rearrangement of the *m*'s or, in other instances with exceeding slowness; but the time element should not mislead us as to the essential characteristics and similarities of the processes.

Intensity and Types of Energy—Many text-books on physics define energy roughly as "the ability to do work," or, what is even worse, as "the *power* to do work." This is a manifest error from the modern point of view as developed by the application of thermodynamics to chemistry; and in the present enunciation of the first law asserting conservation has been avoided. Energy is conserved only when considered as heat and in connection with its ability to produce *heat*. In order that the law of conservation hold, all energy not already heat must be expressed in terms of the one universal form, heat. For instance, a difference in pressure can be made to do work by transforming heat into work; that is, however, merely a direct or postponed transfer of heat and a difference in pressure is not energy in any proper sense of the word. Work is a kind of energy and heat is a kind of energy and, since they are dynamically equivalent, the transformation of one into the other is not energy at all, but a process. Any configuration of a system of bodies by means of which heat may be transformed into work is said to possess energy, *i. e.*, the ability to do work; and this use of the word accords with its historical meaning, but if it is not already heat it exists as work in the scientific sense of potential; hence the growing use of the word potential to supply this need. A configuration of a system—the state of a system—may be utilized to bring about a transformation either into kinetic energy or the energy of position, or strain. There is, however, no exact term, so far as I know, to express the state of a system which lends itself merely to the transformation of heat into work. The distinction by Helmholtz of "free" and "bound' energy

comes the nearest to expressing the sense; but it is only in the historical sense of ability to do work that it is applied and used. What Thomson and Tait meant by energy, as the term was used in their *Natural Philosophy*, is what is now known as potential energy.[1] The entire "free energy" of an isolated system may, under certain circumstances, disappear absolutely without diminishing the total energy of the system one particle. Failure to recognize fully the significance of this peculiar state of a system of bodies and to have a special term which expresses it definitely together with the current, old, historical, but misleading sense of the word energy, has no doubt added much difficulty to the comprehension of energy and led us to suppose that to be energy which is not energy. The word potential applies excellently to the case where energy, other than heat, disappears and heat, or its equivalent in another potential form, takes its place. What we need is a term—one word—to express the state represented by Helmholtz's "free energy"—to express a state of a system favorable to a transformation of heat into work. A term consisting of a single word would enable us to express succinctly the state of a system with reference to its ability to produce or bring about a transformation of one kind of energy into another and I venture to suggest and shall make use of the word *ergon* with that meaning attached. It is evident that ergon is quite a different thing from energy itself. If a difference in temperature were the only kind of ergon, such a term and its use would be unnecessary because the disappearance of the difference of temperature by the performance of work indicates at once the transformation of the heat (which gave rise to the difference in temperature) into work. But from the third law it is seen that in addition to the possession of energy a non-uniform distribution of energy is essential to produce transformation of energy. The possession of ergon by a system is then equivalent to possessing a non-uniform distribution of energy. The ergon itself has no energy equiv-

[1] Notwithstanding the fact they fully developed the doctrine of conservation, they continued to use the term energy in the above restricted sense.

alent; but the second law asserts that the ergonic state never originates of itself in a conservative, isolated system. The ergon disappears with time in a system left to itself. In terms of entropy, the ergon during spontaneous processes, decreases as the entropy increases and approaches zero as the entropy approaches a maximum.

Since there are but two kinds of energy, kinetic and potential, which may be concisely described as energy due to motion and energy due to position or strain, respectively, then in an isolated system we must have

$$\Sigma(K) + \Sigma(P) = H = \text{a constant.}$$

In general, the potential energy $\Sigma(P)$ decreases and $\Sigma(K)$ increases in an isolated system, but a state of a system may exist, temporarily, in which the reverse process is the only one possible; that is, an increase in the $\Sigma(P)$ at the expense of the $\Sigma(K)$, and this may take place spontaneously without affecting the total energy After this process is completed, the reverse process may then, in the absence of external action be the only one possible. Which process takes place will depend on the initial state. The doctrine of the dissipation of energy by Kelvin was based on the fact that what he called energy is the $\Sigma(P)$, above, and which we now call potential energy. The $\Sigma(K)$ he referred to as heat and in an isolated system the $\Sigma(P)$ must ultimately vanish and be replaced by $\Sigma(K) = H$. The term ergon is applicable to either case in which either kind of energy is increasing at the expense of the other. The two cases may be distinguished by opposite algebraic signs; but *all* spontaneous changes are such as to diminish the ergon of a system left to itself.

The application of the preceding principles to the phenomena connected with solutions is evident. A system, consisting of a solution and a pure solvent possesses ergon in addition to energy. The ergon disappears entirely by dilution by equalizing the inequality of the distribution of the energy that gave rise to the ergon. The ergon may disappear spontaneously under favorable circumstances by the passage

of energy from the adjacent solvent to the solution which is depressed in consequence of energy transferred from the solvent to the solute. The difference in the intensity which determines the direction of transfer of the kinetic energy, in the case of the vapor of the pure solvent as compared with the vapor of the solution, is manifested as a difference in pressure instead of as a difference in temperature. The difference is really one of quantity of energy per unit volume; but this may be manifested either as a difference in the number of molecules per unit volume when their average velocities are the same, or as a difference in the average velocities when the number of molecules per unit volume is the same, *i. e.*, a difference in temperature. In other words, a transfer of energy is determined by intensity of kinetic energy, but this difference may be due either to the number of molecules when the temperatures are the same or to the energy per molecule when the numbers are the same.

The whole process of spontaneous dilution is important as throwing light on energy transfers and transformations. The ergon of spontaneous processes may doubtless arise from a great variety of external actions; but when once produced plays an important part in the economy of Nature; for the great majority of energy transfers are mere eddies in the energy stream, *but during transfers of energy transformations take place.*

If the preceding remarks are kept in mind there can be no objection to the use of the terms "*types*" of energy and "*intensity*" of energy. The quantitative equivalence of all types whether potential or kinetic is determined solely by their heat values, as it is only the heat value of an isolated system that is constant. A type of energy may, however, arise from a molecular configuration occurring in a non-uniform distribution that will introduce an energy transfer, but the energy must be actually potential or kinetic. It can have no potential value unless its equivalent in heat appears on its disappearance; and no other claim to be regarded as kinetic beyond the value to which it is entitled in virtue of its

$\Sigma(^1/_2\ n\ m\ u^2)$. If in any process other than a heat transfer, the only change that takes place when work is done is a fall in temperature indicating a change in the average u^2 only, then whatever the character of the kinetic energy, its decrease has been a decrease in heat. Such a process, not a heat transfer, due to the ergonal state of the system, taking place spontaneously, and by which work may be done at the expense of the heat of the system or of the environment, may, in my judgment, properly and without error, be regarded as representing a type of energy undergoing transfer. Likewise, the difference of whatever nature that gives rise to the transfer may be regarded as a difference in intensity. In other words, although heat is the standard by which the quantity of energy must be measured, a difference in temperature is by no means the sole origin of energy transfers; that is determined by the character of the ergon of the system.

It should hardly be necessary to state that an attempt to express our conceptions of the energy processes in formal laws, is in any way to be construed as an attack on the doctrine of entropy, or, as an attempt to dispense with the use of the entropy function; that may still be the best mathematical expression of our present knowledge. In fact, the entropy function is so well established through actual service performed that the only change likely to be made in it will be one of range—to extend its applications rather than to limit them. This, we can see *might* result from a clearer conception of the physical processes that it actually represents, since it has already given such valuable results in so many ways. Before its applications can be limited it will have to be shown that its use leads to erroneous results. That there is, however, a real difficulty arising from the lack of a definite formal statement of the physical significance of the entropy function is evidenced in the great variety of notions current as to what constitutes "entropy." Since there is an entropy function there must be an "entropy." "What is entropy?" is a question with which every teacher of thermodynamics is familiar. My reply to that question has been that entropy

is a mere abstraction, but that the entropy function is a mathematical function that is used to show the changes in the energy state of a system of bodies during energy transfers and transformations. The present paper is an effort to show the reasons for holding such view.

In Professor Planck's excellent treatise, before referred to, on p. 101 there occurs the following remarkable statement that is in direct conflict with the above view, if we may interpret the words as they read. In speaking of diffusion in perfect gases and further dilution of dilute solutions, he says: "Such processes are accompanied by no perceptible transference of heat, nor by external work, nor by any noticeable transformation of energy. They occur only for the reason that they lead to an appreciable increase of the entrophy."

Now if the three laws of energy previously enunciated comprise *all* the fundamental and necessary facts of energy, there is no room for "entropy" as the active agent in any natural process. *All* spontaneous natural processes (not merely the majority of them) are energy processes and these processes are but two,—transference and transformations. Since, then, there is no perceptible transformation in the above-mentioned spontaneous natural processes, there must be a transference of energy of some sort. And the proof that these processes constitute a transference of energy is found in the fact that they may be utilized to do work—that the energy undergoing transfer may bring about a transformation of kinetic into potential energy. The term ergon is particularly adapted to these two processes. The ergon is not a "kind of energy conceived *ad hoc*" to explain a transformation but is merely a term applied to a system that exhibits spontaneous activity. The ergon is not assumed to be a cause of the action but is merely a name, like "entropy," to designate an energy state of a system. To attribute ergon to the system is merely a short and general method of saying that the energy is non-uniformly distributed and that the observed action is rendering the system more uniform by a process of

redistribution. The above quoted curious statement I take to be wholly due to the fact that Professor Planck regards temperature and pressure as complete energy specifications. Indeed, he says so in a footnote reply to a former criticism. It should be distinctly noted in the above quotation that it is claimed only that there is "no perceptible transference of heat"—a statement that cannot be disputed. He apparently takes it for granted that all possible energy changes are eliminated by the assumption of a standard temperature and a standard pressure. Hence it follows, logically, that changes not accompanied by a change in temperature or a change in pressure or both, cannot be energy changes. This conclusion is necessitated by his definition of the standard state. Either this conclusion or a revision of the standard specification is demanded. His conclusion cannot be disputed if his premises are accepted.

Writers have apparently overlooked the fact that there may be exceptions to the above standard. It does not hold, necessarily, except in those cases where there can be no change in density without a corresponding change either in temperature or in pressure, or both. Where a density change is possible without a change in temperature as happens when a perfect gas changes volume without doing work or changing temperature it does not hold. Or when two gases diffuse into each other, the physical change observable, if the mind is unbiassed by molecules, is a change in density without any change in either temperature or pressure. But since a change in density *is* an energy change when accompanied by either temperature or pressure change why is it not also when these accompaniments are absent? The only answer seems to be that the mind becomes biassed through the supposed relation of cause and effect. It is never safe to assume that one natural action is the cause of another. A change in density is attributed to the change in pressure. What objection can there be to regarding the change in pressure as due to the change in density? Experimentally the former is the obvious; but theoretically, from the kinetic theory the change in the

density is the cause of the change in pressure, as the term is applied to gases. During diffusion, the separate species of molecules are afforded additional space and the substance undergoes a corresponding change in density. The sum of the separate pressures is not altered, except temporarily, by the process of diffusion, but the separate densities are changed. Theoretically, it would seem necessary to regard density as the cause and pressure as the effect, for by such view we bring within the pale of the entropy function phenomena hitherto regarded as sporadic.

If, as assumed at the beginning of this discussion, the entropy function represents the fundamental equation of condition that *must be satisfied* under all the varying conditions of spontaneous natural actions and the three assumed laws also represent correctly the same natural actions, then the two expressions of the same actions must be consistent. There can be no exceptions. Both should then give a satisfactory result when applied to the expansion of a perfect gas into a vacuum and to the phenomena of the interdiffusion of two fluids when interpreted by considering both the function and the laws. From the point of view of the laws, the expansion of a gas into a vacuum is a pure transfer without any accompanying transformation. The entropy function should then show an increase in value if it is to be interpreted as increasing with transfer and decreasing with transformations into potential forms—since, in this case there is no transformation, but transfer only.

The usual form of the entropy function is

$$d\phi = \frac{dU + Pdv,}{\theta}\text{, or, } \phi_2 - \phi_1 = \int_1^2 \frac{dU + Pdv}{\theta}$$

with the usual meaning of the symbols.

If we attempt to apply this function to the case of a gas expanding into a vacuum we are met at the outset by apparent difficulties. Both $d\,U$ and $P\,dv$ become zero between any two proposed limits while θ remains constant. As

ordinarily interpreted, the integration leads merely to a constant; and since both the internal energy and the temperature remain constant during the process, this result has been accepted without attracting the attention it would have received had the result not been so *apparently* reasonable. Although Pdv is supposed to represent work, it is really a symbolic expression for energy, including mechanical work as *one* of its possible meanings; but it may have possibilities not contemplated when assigned this evident duty. In the present case dv is not zero but P is apparently discontinuous. However, remembering that the density cannot be discontinuous and that the mass is constant, we have $M = \rho v$, and from the general gas equation, by substitution, we have $P = \rho R\theta$. Then from $M = \rho v$ we have $\rho dv = -v d\rho$. By substituting and integrating we get

$$\phi_2 - \phi_1 = \int_{\rho=\rho_1}^{\rho=\rho_2} -MR\frac{d\rho}{\rho} = -MR\log_e\frac{\rho_2}{\rho_1} = MR\log_e\frac{v_2}{v_1}$$

the same result that is obtained for the entropy *change* by special methods that are regarded as rigorously true. The above method might be open to doubt were it not supported by the *result*. However, the same result may be obtained from purely mathematical considerations.

The history of mathematics affords many instances of analytical value obtained merely by our being compelled to extend the significance of our symbols in order to interpret the results of our analysis. Pdv is supposed to represent work done on or by the gas. If done by the gas the algebraic sign is conventionally negative; if done on the gas, positive. In this convention there is no provision for *negative work done by the gas*. If we suppose such a contingency possible, the negative result would have to be subtracted; hence writing for P its value expressed as $\frac{MR\theta}{v}$ we get $\frac{P\,dv}{\theta} = MR\frac{dv}{v}$ which on integration gives the same result as before, *but it must be interpreted as negative work done by the gas*. Physically, this

can be interpreted as the external work necessary to restore the original state.

The same methods are available in connection with interdiffusion of two gases and lead to the result obtained by special, and what are regarded as, rigorous methods. By inversion of the usual order of deduction we may conclude that the reasoning by which the results are obtained, is valid because it leads to correct results. It is claimed that Hamilton used this method of reasoning in establishing the conventional use of the symbols required while developing his system of quaternions.

It would seem then that the specification of a standard energy state in terms of temperature and pressure should be supplemented by the proviso that no change in density takes place that cannot be accounted for in terms of temperature and pressure. In other words, *the density must be a function of the temperature and pressure in order that a specification in terms of temperature and pressure shall hold.* This is generally true but, as we have seen not always true. A specification in terms of temperature and density is all that is required to remove this exception to the general law. The warrant for this change may be found in the fact that from the kinetic point of view, density is the antecedent "or cause" and pressure is the consequent or "effect." Externally applied pressure is a measure merely of *average* density, not actual. Also, since mass is the product of density and volume, it would seem that density is a more fundamental fact than pressure.

That the change in the entropy attributed to the interdiffusion or mixing of two gases is not due to the mixing but to the change in volume and consequent change in density of the separate constituents is easily demonstrated.[1] The change in entropy is attributed to the mixing; but he disproves this statement by separating them without change of entropy. Therefore, the entropy change is entirely due to

[1] For proof see Planck, loc. cit., p. 211.

the redistribution, or change of volume, of the separate constituents, or types of energy, and not to the inter-mixing of the constituents. This proof is conclusive and furnishes additional warrant for regarding the entropy change during expansion into a vacuum as due to a pure transfer unaccompanied by transformation, as also holds during interdiffusion. The same reasoning may evidently be applied to liquid diffusion and to solutions. For, an ergon due to a temperature difference, may be produced by salt-ice as well as by means of coal. Also, if a selective membrane could be found that would separate the rapidly moving molecules from the slower moving ones in a homogeneous fluid (Maxwell's demon) this would not contradict any of the laws of energy—merely enable us to produce an ergon by which kinetic energy could be transformed into potential energy. Without an ergon this is impossible. Such a membrane, or Maxwell's demon would merely enable us to do what we may now do by means of a soluble substance or a piece of ice; such devices would enable us to give rise to an ergon by producing a difference in the average mo ecular velocities in the adjacent portions of an otherwise homogeneous fluid. In either case, the ergon is due to external agency, *i. e.*, is not produced spontaneously. Selective membranes *do separate* molecules of different velocities when the molecules also possess different masses, *i e.*, are of different species. The principle would not differ if they were of the same species; in either case the ergon is equivalent, either directly or indirectly, to a temperature difference; and a temperature difference may be utilized to do work. Fuel enables us to produce a temperature above the general level and do mechanical work. A sufficient supply of salt-ice would be economically valuable during summer temperatures by enabling us to do work or produce high temperatures by means of the heat of the environment.

Another test of the validity of the conceptions embodied in the proposed formal laws may be obtained by comparing the original function with energy and with the results found for a *change* in the value of the entropy function due to a

pure transfer. The canonic value for the entropy change just found has the dimensions of energy per degree. But as temperature is a dimensionless quantity in terms of length, mass, and time, the dimensions of a change of entropy are the same as the dimensions of energy. The value just found may be written $\frac{Pv}{0}\log\frac{v_2}{v_1}$. It is evidently energy per degree multiplied by a dimensionless factor, $\log\frac{v_2}{v_1}$. The change of entropy due to the conduction of a quantity of heat, Q, from the temperature θ_1 to θ_2 may be expressed in the form of energy per degree multiplied by a dimensionless ratio. If the quantity of heat Q passes abruptly from the temperature θ_1 to the temperature θ_2 the *change* in the entropy is evidently $\frac{Q}{\theta_2}-\frac{Q}{\theta_1}=\frac{Q}{\theta_1}\left(\frac{\theta_1-\theta_2}{\theta_2}\right)$. But if it is transferred by conduction and is uniformly distributed between the temperature θ_1 and θ_2 (*i. e.* with a uniform temperature gradient, as while passing through a conducting wall) the value of the entropy of the total heat *in* the wall lying distributed between θ_1 and θ_2 will be

$$\int_{\theta_1}^{\theta_2}\frac{dQ}{\theta}=Ms\int_{\theta_1}^{\theta_2}\frac{d\theta}{\theta}=Ms\log\frac{\theta_2}{\theta_1}=\frac{Q}{\theta_o}\log\frac{\theta_2}{\theta_1}$$

if we write $Msd\theta$ for dQ and $Q=Ms\theta_o$ where M is the mass of the wall, s the average specific heat, and θ_o represents the temperature to which the heat Q would raise the wall if the heat were uniformly distributed. In both cases we have heat per degree into a dimensionless factor. The result is even more striking when we recollect that, in a perfect gas, for equal pressures $\frac{\theta_1}{\theta_2}=\frac{v_1}{v_2}$. The conduction of heat and the expansion of a gas without doing work seem to have similar energy characteristics.

Now if entropy change is measured in energy per degree during pure transfer, then also during complete transformation as in reversible processes, when there is no change of entropy

there should be no change in the energy per degree when all the heat of the working substance that disappears is transformed into work. For illustration we may use the simplest case, that of a perfect gas where the internal kinetic energy is proportional to the absolute temperature. Let $\frac{Q}{\theta}$ represent the energy per degree of a perfect gas. From the mathematical principle that a ratio is unchanged by increments to the terms bearing the same ratio as the original ratio, we must have

$$\frac{Q \pm \Delta Q}{\theta \pm \Delta\theta} - \frac{Q}{\theta} = 0$$

for all values that make $\frac{\Delta Q}{\Delta\theta} = \frac{Q}{\theta}$. But if $\Delta Q = \Delta W$ by the first law, the work done during expansion by the cooling of the gas, then $\Delta W = Q\frac{\Delta\theta}{\theta}$, one of the fundamental equations of thermodynamics based on reversible cycles. However, one marked distinction between energy per degree and entropy, during reversible cyclic processes is noticeable in Carnot's cycle. The energy per degree of the working substance is constant for all four processes while in the usual treatment the heat supplied or withdrawn is regarded as changing the entropy. Since these are different in consequence of the work done, $Q_1 - \Delta Q = Q_2$ and $\theta_1 - \Delta\theta = \theta_2$ or, by the above principle, $\frac{Q_1}{\theta_1} = \frac{Q_2}{\theta_2}$ if $Q_1 - Q_2 = W$. Counting the heat added or abstracted, however, does not change the *form* of heat per degree; neither has there been any final change in the heat per degree since that is kept constant throughout the four processes.

But aside from the insight into thermodynamical processes that we may obtain from a formal statement of the physical significance of energy processes, a greater advantage is obtained by our ability to put into words the conceptions we may form as to the processes of Nature without having to rely on an abstruse differential equation, however exactly it may represent symbolically the various phenomena that

pass before our vision. Even great mathematicians may form misleading conceptions from their symbols. Lord Kelvin was impressed by what struck him as the general trend of the energy processes and announced the dissipation of energy. While undoubtedly true as a rational proposition, it is yet misleading in its effect on the general mind. The same general doctrine, differently expressed, was enunciated by Professor Clausius, and while representing a physical law in a certain sense, is also misleading in its implications. It is undoubtedly true that in an isolated conservative system a uniform distribution of the contained energy corresponds to a state in which the entropy is a maximum; it can be neither increased nor diminished by any interaction of the constituent parts. The only possible way in which the total energy and entropy can be changed is by giving out or receiving energy. In a non-uniform distribution of the energy of such a system, however, it may proceed by various intermediate steps of partial equilibrium (one or more types balanced against others); but each successive disturbance of the partial equilibrium by other than strictly reversible processes, must increase the actual existing value of the entropy function because the distribution of the energy of an isolated, conservative system is always towards, never away from, uniformity of distribution of the contained energy of the system. The earth, however, considered by itself as a part of the solar system is by no means an isolated conservative system. The periodic reception of energy at any given point on its surface through radiation from the sun, alternating with the same periodic, but not simultaneous, giving out of energy, is the most highly favorable condition for transformations occurring during transfer. On the earth's surface, the condition prevailing during the earlier geologic ages was one of greater uniformity in type and of a much more nearly uniform distribution of energy than exists at present. The present complexity, heterogeneity, the life-processes—evolution—the up-building of complex energy forms, all result from the varying influx and efflux of energy due to processes not

dependent on the earth's own store of energy. The great puzzle—the dynamics of the evolution of life and intelligence on the surface of the earth—could be understood, it is said, as "natural" if it were a running down process; but it is evident to all that what we actually observe is a state of up-building—the complex, heterogeneous and highly organized replacing the simple and homogeneous. If for the misleading statement that "the entropy of the universe tends to become a maximum," or the equally misleading notion that energy is continually "dissipated" we substitute the conception applicable to the earth as an energy system, that it is only during spontaneous, natural transfers of energy that transformations in type take place, the dynamical aspects of the evolutionary process with its continually increasing complexity and diversity of type become comprehensible to us to the extent, at least, of harmonizing our rational experiences.

State College, Pa.,
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EFFECT OF SOLUBLE SALTS ON THE ABSORPTION OF PHOSPHATES BY SOILS[1]

BY HARRISON E. PATTEN

Introduction

In several previous bulletins from this department[2] the absorption of soluble bodies from solution by soils has been exhaustively treated, together with the physical and chemical conditions which are produced by absorption processes. The foregoing work has, however, been confined to the study of the effect of a single dissolved body (solute) on the soil. While there are in the literature a few cases in which the effect

[1] Published by permission of the Secretary of Agriculture.

[2] Some Physical Properties of Soils in their Relation to Moisture and Crop Distribution: Milton Whitney, Bull. No. 4, Weather Bureau, U. S. Dept. Agric., 1892; Fluctuations in the Level and Rate of Movement of Ground Water, F. H. King, Bull. No. 5, Weather Bureau, U. S. Dept. Agric., 1892; The Mechanics of Soil Moisture, Lyman J. Briggs, Bull. No. 10, Division of Soils, U. S. Dept. Agric., 1897; Capillary Studies, etc., Lyman J. Briggs and Macy H. Lapham, Bull. No. 19, Bureau of Soils, U. S. Dept. Agric.; Application of the Theory of Solution to the Study of Soils, Frank K. Cameron, Reprint from Report No. 64, Dept. Agric. Field Operations of 1899, (1900); Investigations in Soil Fertility, Milton Whitney and F. K. Cameron, Bull. No. 23, Bureau of Soils, 1904; The Aeration of Soils, Edgar Buckingham, Bureau of Soils, U. S. Dept. Agric., 1904; The Mineral Constituents of the Soil Solution, Frank K. Cameron and J. M. Bell, Bureau of Soils, Bull. No. 30, U. S. Dept. of Agric., 1905; The Absorption of Phosphates and Potassium by Soils, Oswald Schreiner and Geo. H. Failyer, Bull. No. 32, Bureau of Soils, U. S. Dept. Agric. (1905); Studies on the Movement of Soil Moisture, Edgar Buckingham, Bull. No. 38, Bureau of Soils, U. S. Dept. Agric., 1907; The Moisture Equivalent of Soils, Lyman J. Briggs and John W. McLane, Bull. No. 45, Bureau of Soils, U. S. Dept. Agric., 1907; Moisture Content and Physical Condition of Soils, Frank K. Cameron and Francis E. Gallagher, Bull. No. 50, Bureau of Soils, U. S. Dept. Agric., 1902; Absorption of Vapors and Gases, Harrison E. Patten and Francis E. Gallagher, Bull. No. 51, Bureau of Soils, U. S. Dept. Agric., 1908; The Action of Water and Aqueous Solutions upon Soil Phosphates, F. K. Cameron and J. M. Bell, Bull. No. 41, Bureau of Soils, U. S. Dept. Agric., 1907; The Action of Water and Aqueous Solutions upon Soil Carbonates, F. K. Cameron and J. M. Bell, Bull. No. 49, Bureau of Soils, U. S. Dept. Agric., 1907; Absorption by Soils, Harrison E. Patten and William H. Waggaman, Bull. No. 52, Bureau of Soils, U. S. Dept. Agric., 1908.

upon the absorption of one soluble body produced by the presence of a second soluble body has been studied, no systematic attempt in this direction has been made with soil as the absorbing body.

The present paper deals with experimental evidence showing that the effect of a second solute upon the absorption of a first solute is marked and worthy of consideration both as to its effect upon the retention of the first soluble body and as to its effect upon the physical condition of the mass of soil through which the liquid percolates during absorption or leaching experiments.

Some indication of the effect which might be expected when a second solute is introduced into a solution kept in contact with soil may be obtained from the following considerations which are taken mainly from the work of J. M. Van Bemmelen.[1]

An absorbing body can absorb from homogeneous solutions two or more substances at the same time. Thus for example 1 gram-molecule of the hydrogel of manganese dioxide absorbs from aqueous solution 0.21 gram-molecule calcium oxide, together with 0.11 gram-molecule of ammonia. Within certain limits, in general, in very dilute solution the full amount of each dissolved material is absorbed which the solid would otherwise absorb. That is to say, each substance is absorbed independently without affecting the quantity of the other. But in concentrated solutions the masses which are absorbed are dependent upon the kind, concentration, and number of dissolved bodies. If an absorbing body has come to equilibrium w th a solution containing a concentration C_1 of dissolved material, and a second substance of concentration C_2 s brought into the solution, then partial substitution of C_1 by C_2 may take place, in which the greater absorptive power of the body for C_1 or for C_2 comes into play. This action must frequently be complicated since C_1 and C_2 by mutual interaction may change their solubility in the liquid

[1] Absorption, p. 441, Dresden (1910).

which occupies the spaces of the absorbing body. For example, hydrochloric acid lowers the solubility of potassium chloride in water, and might be expected to affect the absorption of potassium chloride from aqueous solution by solids. But it must be remembered that usually the salt content of the solutions dealt with in absorption studies is far below the saturation concentration; and of course no question of solubility can enter the problem until the solution becomes saturated with solute at the temperature under consideration.

These cases where a salt affects the absorption of a second salt have not yet be n systematically investigated either for gels or for porous, amorphous substances; only general considerations have been made regarding them. Jellied precipitates which contain an acid or a base of a salt in absorbed condition may be much more quickly washed out with a solution (for example, of a salt) than with pure water. When water will not take out more of the remaining absorbed material in the gel then this residuum may still further be extracted with the solution. Van Bemmelen found this to be the case in the following experiments: Using a solution of potassium chloride or potassium sulphate the extracted aluminum chloride from silicic acid gel, sulphuric acid from red manganese dioxide gel, and calcium chloride from chromic oxide gel. Linder and Picton made a similar observation. A small mass of barium hydroxide which had been absorbed by arsenic trisulphide and which could not be further extracted with water, was again brought into solution by treatment with calcium nitrate solution. Likewise calcium hydroxide was brought into solution by use of cobalt solution, and conversely.

Some cases have been investigated in which chemical substitution takes place, for example when the liquid in the gel precipitate already contains an absorbed base and then readjusts itself to equilibrium with the solution of a salt of another base. The bases may n this case to a certain extent undergo substitution. Thus Van Bemmelen found that

silicic acid absorbed caustic potash quite strongly, and also calcium hydroxide. But on the other hand potassium chloride was taken up very little more than corresponded to the solubility of potassium chloride in the water contained in the gel. If now silicic acid which contains calcium oxide absorbed is treated with a solution of potassium chloride, then potassium substitutes the larger quantity of calcium in the liquid of the gel and the chlorine remains where it was originally, in solution. If one applies the ion theory to this, then the absorbing network of gel is in contact with

$$2K \ldots\ldots\ldots\ldots\ldots\ldots 2Cl$$
$$1Ca \ldots\ldots\ldots\ldots\ldots\ldots 2(OH)_2$$

then 2KOH is absorbed and there remains in the solution Ca and 2Cl. An equilibrium results between the liquid in the gel with its absorbed potassium and calcium (along with a small amount of potassium chloride dissolved in the gel water) and the liquid outside of the gel with its concentration of potassium chloride and calcium chloride—or according to the conflicting solution and absorbing tensions and according to the concentration of which the solution and absorption tensions in turn are a function.

Experimental Work

The aim of the experimental work undertaken in this research was first to establish the effect of the second solute upon the absorption of the first solute, using one chemical substance of known composition as a solid; and second to extend the observations to the case of the more complex solid absorbing bodies, such as soils. The single-substance solid taken was crushed quartz, about 83 percent of the size known as silt and 17 percent clay size. The soils taken were Podunk fine sandy loam and Elkton clay.

In this paper attention has been confined to the effect of various salts, sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), potassium chloride (KCl), potassium sulphate (K_2SO_4), and potassium carbonate (K_2CO_3) upon the quantity of phosphate (PO_4) which could be leached from a known

weight of soil treated with calcium mono-phosphate (equivalent to 350 pounds of superphosphate per acre), when percolated with water or with the aqueous solutions just mentioned.

Method of Analysis.—The percolates from the various soils were acidified by using a few cubic centimeters of strong nitric acid with 50 cc of percolate, and allowed to remain upon the steam bath for some 24 hours to render the silica insoluble. The residues were then extracted with very dilute nitric acid, filtered from silica, and again evaporated to dryness in platinum. They were then ignited at a low, red heat to destroy any organic matter. Finally the residue was treated with dilute nitric acid as directed under the colorimetric method for phosphates, described in the bulletin on Colorimetric and Turbidity Methods, of this Bureau.[1] The color for phosphates was developed according to this method and the concentration in parts per million PO_4 was calculated to that of the original percolate from this soil, whose volume was in every case accurately measured in cubic centimeters. The complete removal of silica from these percolates by the above method of treatment is well shown in the case of the percolates low in phosphate; these solutions passed through large quantities of silica in the soil, and yet the final residues obtained from evaporating in platinum showed extremely low concentrations of phosphate when developed colorimetrically.

Results.—Table I shows the effect of percolating 100 grams of quartz flour treated with 0.061 gram of calcium mono-phosphate ($CaH_4(PO_4)_2$). The various headings in the table are self-explanatory, with perhaps the exception of the division of Table I into two parts (1) and (2), which are duplicates. These in turn are divided into two parts, the lower showing the effect due to the passage of aqueous solution of sodium nitrate ($NaNO_3$) 0.05 percent, instead of the distilled water. The striking fact brought out in Table I is

[1] Schreiner and Failyer: Bull. No. 31, Bureau of Soils, U. S. Dept. Agric. (1906).

that at concentrations of phosphate far below the solubility of the quantity of phosphate added to the quartz in the volume of liquid passed, only from 6–20 parts per million of phosphate is evident in the leachings after some 90 cc of distilled water have passed, and this is maintained probably up to 200 cc of solution leached. But when the sodium nitrate solution is passed Fig. 1, the concentration of phosphates

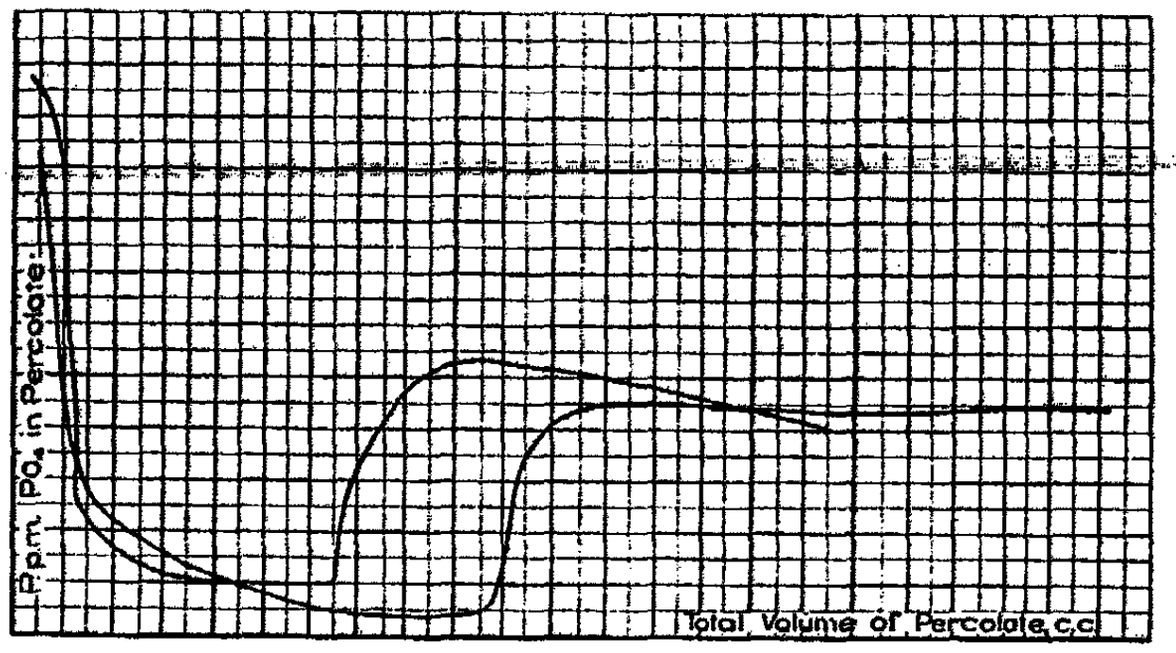

Fig. 1.—Leaching curve of crushed quartz with calcium monophosphate, and then percolated first with distilled water, and then with sodium nitrate solution, 0.05 percent

in the leachings immediately rises and remains fairly constant at between 40 and 50 parts per million. The duplicate experiment (2) shows the same effect, although the total quantities of leached solution are not quite the same and its percolation rate is considerably different from the rate shown in (1). Thus it is evident that the addition of a very small amount of nitrate to the quartz flour containing absorbed phosphate facilitates the passage into a leached form of something like three times as much phosphate as is obtained by distilled water alone.

In Table II, under headings of the same style as those used in Table I, are given the data for the leaching of phosphate from 100 grams Podunk fine sandy loam treated with 0.061 gram of calcium mono-phosphate. Section No. 1

shows the leaching effect of distilled water, section 2 that of a 0.05 percent sodium nitrate solution, section 3 that of a 0.1 percent solution of sodium nitrate, section 4 that of a 0.5 percent potassium sulphate solution, section 5 that of a 0.5 percent potassium chloride solution, and section 6 that of potassium carbonate. In Table II the various sections are each independent experiments, starting with 100 grams of soil, to which was added 0.061 gram of calcium mono-phosphate, moistened, and the absorption process allowed to go on for two days; after which each soil was percolated with the solution indicated under each section in Table II. In comparing the concentrations of phosphate which were leached by these different solutions, one must take into consideration the rate at which each solution percolated through the soil. In general all of the salt solutions, with the exception of potassium carbonate, accelerated the rate of percolation; however, in spite of this increased rate at which the liquid passed through the soil, inspection of Table II shows that a somewhat higher concentration of phosphate is found in the leachings when these salts are used than the concentration of phosphate given by leaching with distilled water alone, Fig. 2 and Fig. 3. Take for example the case of potas-

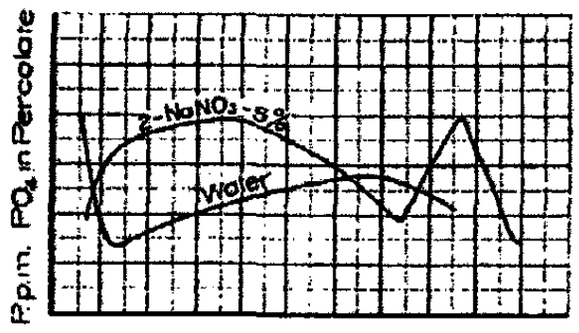

Fig. 2.—Leaching curves for Podunk fine sandy loam treated with calcium mono-phosphate, and percolated (1) with water and (2) with sodium nitrate solution, 0.05 percent

sium sulphate: Here the rate of leaching after some 300 cc have passed is over three times as great as the percolation rate for distilled water, yet the concentration of phosphate is about the same as that given by distilled water. Con-

versely, for the percolation of potassium carbonate it will be noticed that the parts per million of phosphate in the leachings ascend continually while the rate of percolation decreases nearly to zero. Comparing the results in Tables I and II, it is seen that each percolating solution after a time appears to approach equilibrium in a general way (save in the

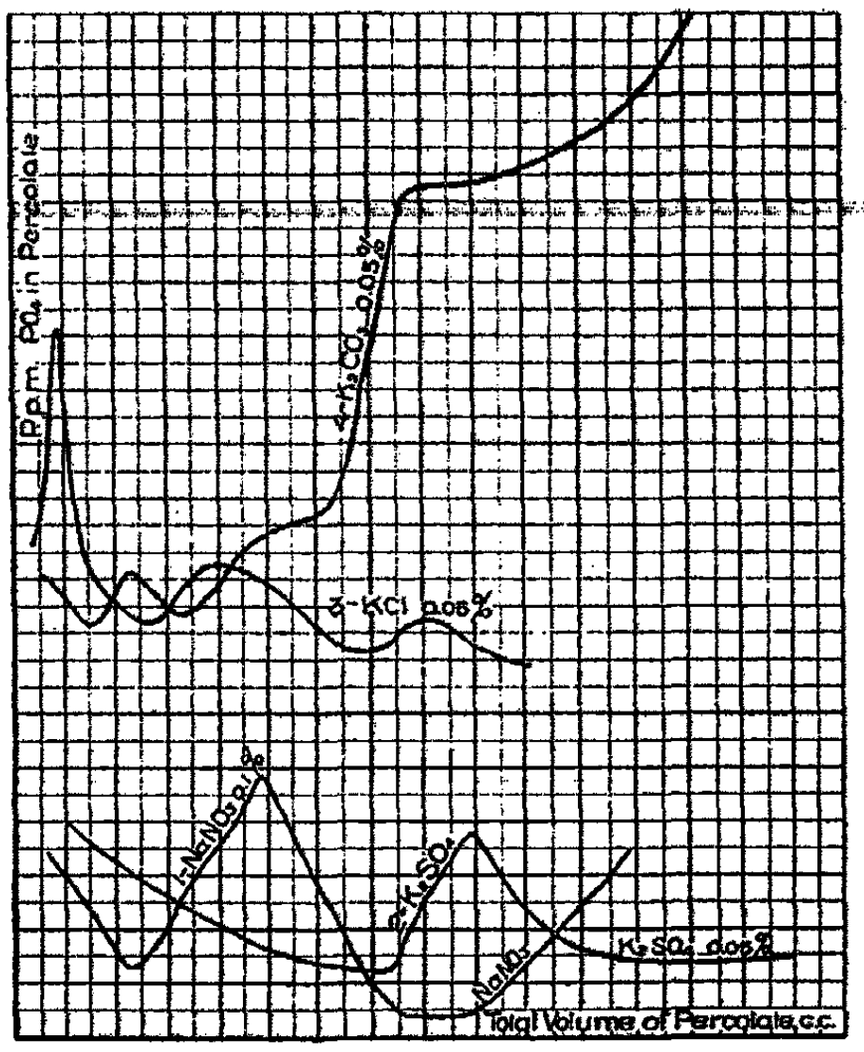

Fig. 3.—Leaching curves for Podunk fine sandy loam treated with calcium mono.phosphate, and percolated (1) with sodium nitrate solution, 0.1 percent; (2) with potassium sulphate solution, 0.05 percent; (3) with potassium chloride solution, 0.05 percent; and (4) with potassium carbonate solution, 0.05 percent

case of the potassium carbonate). The percolation rate tends to become steady, and the concentration of phosphate in the leachings also tends to become steady (throwing out of consideration variations in the results for the concentration, which may readily be due to the alteration of soil structure

under percolation conditions due to rearrangement of soil particles as the solution bathing them increases or decreases in concentration, with consequent readjustment of the approximate equilibrium between the absorbed material on soil grains and the dissolved material in solution). The slowing up of the percolation in the case of potassium carbonate is due[1] to the disaggregation of soil particles under the influence of this alkali (a general phenomenon), and consequent clogging of the pore spaces by this single-grained submicroscopic material.

While it is probable that the soil organic matter plays a part in action such as that indicated by these experiments, it by no means functions as the conditioning factor, since with quartz powder containing no organic material we have this effect of one solute upon the adsorption of another strongly marked. Both the soils used were low in organic material; the total organic matter found was approximately 0.66 percent for Elkton clay and 0.37 percent for Podunk fine sandy loam.

Table III extends the observations given above for Podunk fine sandy loam to cases where we have a larger quantity (250 grams of soil) with a corresponding quantity of calcium mono-phosphate, 0.1525 gram, the dry mixture being wetted, thoroughly stirred, and allowed to dry out to a dusty powder, after which it was dropped into cylindrical tubes about four and one-half cm internal diameter, the soil bed being about 12 cm in depth, depending upon its condition of packing. Distilled water or aqueous solution as indicated in the sections below was passed through this soil bed and its rate of percolation, total cubic centimeters of percolate, and concentration of phosphate determined. The percolation rate in every case is slower than for the smaller quantity of this same soil used in Table II, as would be expected. The concentrations in phosphate likewise are higher for distilled water alone. This also would be expected under a slower rate of percolation. The effect of the potassium nitrate in solution is clearly in evidence in both the 0.1 per-

[1] Compare the studies on leaching of black alkali given in Bull. No. 52, Bureau of Soils, U. S. Dept. Agric., p. 75 (1908).

cent and the 0.05 percent solution, and shows even more clearly than in Table II, as might well be expected since the contact of solution with soil material is of greater duration, Fig. 4.

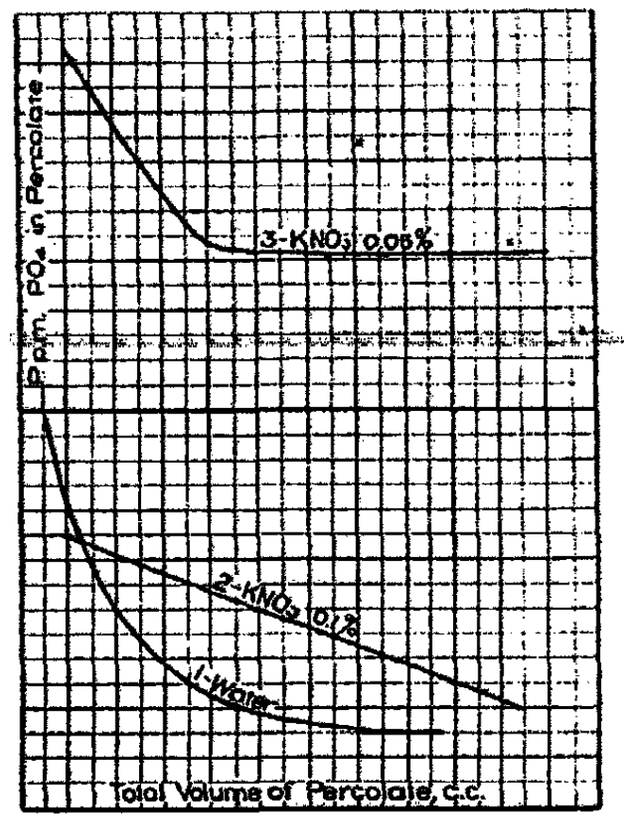

Fig. 4.—Leaching curves for Podunk fine sandy loam treated with calcium mono-phosphate, and percolated (1) with water, (2) with potassium nitrate solution, 0.1 percent, and (3) with potassium nitrate solution, 0.05 percent

In Table IV are given the data obtained using 250 grams of Elkton clay, treated with 0.153 gram of calcium mono-phosphate. The data given in the first section show the effect of distilled water alone, the percolation rate being of course very much slower than in the case of the quartz flour or Podunk fine sandy loam. The results given in section 1 and in section 2 are for independent experiments, using different samples of this same soil, Elkton clay. The lower part of section 2 shows the leaching effect produced by the addition of a 0.05 percent sodium nitrate solution. Its effect is not so marked as in the case of the Podunk fine sandy loam, but we have nevertheless a suggestion of its effect in the concentration of phosphate given as 12.7 parts per million.

One reason for this lack of effect of the second solute ($NaNO_3$) may be due to the high absorptive power of the clay for nitrate, the clay possibly being able to retain both nitrate and phosphate at the concentration of nitrate supplied in the percolating solution.

Section 3 of Table IV is a third leaching of Elkton clay, treated with calcium mono-phosphate using distilled water alone. After 329 cc of percolate have passed, a 0.05 percent solution of potassium chloride was run through the soil, instead of the distilled water, and after a time its effect became evident in the higher concentrations of phosphate as well as in the greater speed of percolation, Fig. 5.

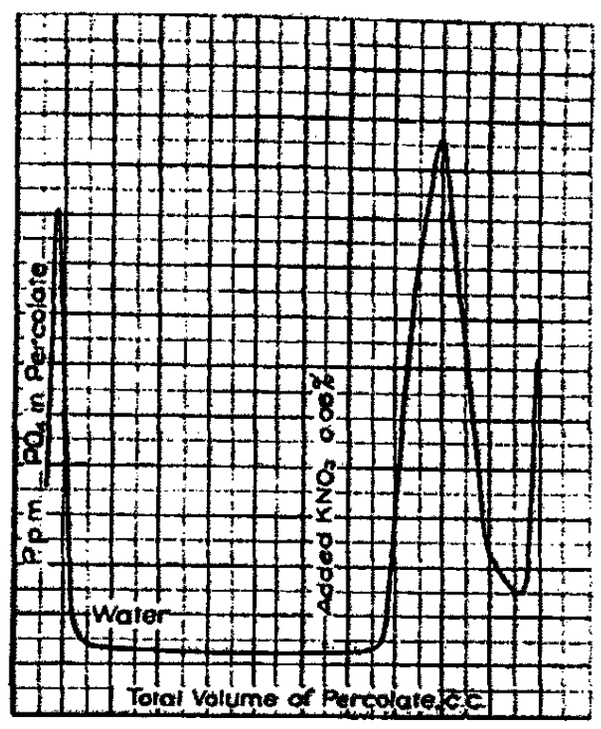

Fig. 5.—Leaching curves for Elkton clay, treated with calcium mono-phosphate and percolated (1) with distilled water, (2) with potassium nitrate 0.05 percent

Table V shows the concentrations of phosphate which were obtained by leaching 250 grams of Elkton clay as taken from the sample, without addition of calcium mono-phosphate, Fig. 6. The phosphate content in general is much lower than that obtained either by the distilled water alone passed through a phosphate-treated soil or by the use of a second solute to liberate the phosphate.

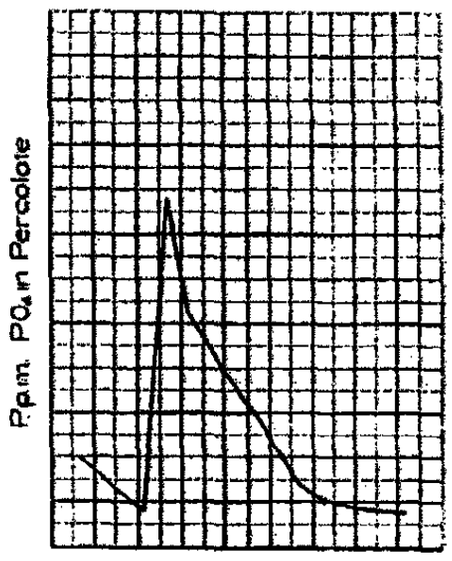

Fig. 6.—Leaching curve, Elkton clay, untreated.
Percolated with distilled water

Conclusions

From experiments with a single substance, quartz, and with two soils, one an open, sandy soil and the other a fine clay, it appears that a higher concentration of phosphate may be obtained when weak solutions of salts ordinarily used as soil amendments (potassium chloride, potassium sulphate, potassium and sodium nitrate, or potassium carbonate) are passed through the soil than can be obtained by the use of distilled water alone.

This effect is not simply a question of the "solubility" of phosphate in water or in the solutions used for percolation, since the volume of water held in contact with the soil material is in all cases far greater than that required to dissolve the small amounts of phosphates and of other salts present. The effect is evidently due to a disturbance and rearrangement of the equilibrium which exists or tends to exist between the soluble material retained by the soil, and the soil solution. This disturbance of equilibrium having been produced by these soil-amendment salts again tends to readjust itself, giving (*very roughly*) a steady value for the concentration of the leachings.

The absolute values of phosphate concentration in the various percolates are not to be taken as representing what

would be obtained under field condition with these soils. The values are good only in the particular experimental environment and in comparison with each other; and even then are likely to be misinterpreted if one neglects the percolation *rate* and the irregularity of soil-percolation conditions. The effects of the liberated phosphates and of the added soil-amendment salt upon the physical structure and condition of the soil must likewise be considered. These effects are generally of considerable magnitude, and frequently so complicated that it is impracticable to predict their direction *a priori*.

TABLE I

100 grams quartz flour with 0.061 gram $CaH_4(PO_4)_2$

Percolation rate cc per min.	Total volume of percolate cc.	PO_4 in percolate p. p. m.
(1)	Distilled water	
0.00981	10	93
0.00892	23	36
0.00901	36	22
0.00846	51	19
0.00834	63	—
0.00853	84.5	...
0.00925	111.5	6
0.01097	126.5	7
0.01017	156.5	4[1]
0.0102	170.0	—
0.0081	194.0	7
	Sodium nitrate solution, 0.05 per cent	
0.00935	209	36
0.0080	242	50
0.0084	265.5	44
0.0084	289.5	43
0.0091	331.5	40
0.0088	367.5	43
0.0092	408.5	44
0.0070	447.5	44

[1] The soil drained over night so that no standing water remained above it, consequently the rate of percolation is uncertain.

TABLE I—(*Continued*)

Percolation rate cc. per min.	Total volume of percolate cc.	PO_4 in percolate p. p. m.
(2)	Distilled water	
0.0069	7	108
0.0062	16	102
0.0062	25	24
0.0059	35.5	—
0.0056	43.5	—
0.0052	56.5	—
0.0060	74.0	10
0.0069	83.5	10
0.0061	101.5	10
0.0072	110.5	—
0.0066	130.5	11
	Sodium nitrate solution, 0.05 per cent	
0.0072	142.0	33
0.0060	167.0	50
0.0063	185.0	54
0.0063	203	48
0.0069	235	51
0.0067	262	55
0.0067	292	44
0.0060	325	42

TABLE II

100 grams of Podunk fine sandy loam with 0.061 gram $CaH_4(PO_4)_2$

Percolation rate cc. per min.	Total volume of percolate cc.	PO_4 in percolate p. p. m.
(1)	Distilled water	
2.25	9	21
2.17	22	7
2.27	39	8
1.52	61	11
2.30	84	11
1.96	108.5	14
2.19	133.5	13
1.81	157	9
1.53	180	
1.28	203	—
0.94	227.5	—

(2) Sodium nitrate solution, 0.05 per cent		
1.78	12.5	20
2.00	28.5	18
2.00	48.5	18
2.08	73.5	20
1.92	97.5	17
2.08	121.5	14
1.96	146	9
1.85	171	20
1.93	198	7
(3) Sodium nitrate solution, 0.1 per cent		
2.4	12	17
2.78	24.5	13
2.63	45.5	6
2.55	71	lost
2.65	97.5	24
2.70	124.5	11
2.52	151	2
2.76	180	2
2.76	209	9
2.80	237	17

TABLE II—(*Continued*)

100 grams of Podunk fine sandy loam with 0.061 gram $CaH_4(PO_4)_2$ percolated with various solutions

Percolation rate cc. per min.	Total volume of percolate cc.	PO_4 in percolate p. p. m.
(4) Potassium sulphate solution, 0.05 per cent		
2.91	14.5	21
3.25	34	14
3.33	59	15
3.41	88	9
3.34	118	7
2.76	147	6
3.21	177.5	19
2.59	208.5	9
3.10	239.5	7
3.24	273.5	7
2.80	301.5	8

TABLE II—(*Continued*)

Percolation rate cc. per min.	Total volume of percolate cc.	PO_4 in percolate p. p. m.
(5)	Potassium chloride solution, 0.05 per cent	
2.28	8	16
2.37	17.5	36
2.20	34	12
2.44	53.5	8
2.50	78.5	14
2.46	105.5	11
2.21	132	5
2.29	159.5	9
2.19	188	5
2.20	215.5	4
(6)	Potassium carbonate solution, 0.05 per cent	
1.75	10.5	13
1.67	30.5	8
1.69	44	13
1.55	68	9
1.42	93.5	16
1.27	121.5	18
1.07	153.0	48
0.69	184.5	49
0.46	198.5	54
0.147	223.5	
0.0185	253.5	130
0.0055	258.5	—

TABLE III

250 grams of Podunk fine sandy loam with 0.1525 gram $CaH_4(PO_4)_2$ percolated with various solutions

Percolation rate cc. per min.	Total volume of percolate cc.	P_2O_5 in percolate p. p. m.
(1)	Distilled water	
0.253	9	39
0.349	20	22
0.358	37	24
0.324	58.5	19
0.242	77.5	9
0.206	103.5	5
0.147	113.5	11
—	120.5	13
0.143	144.5	6

(2) Potassium nitrate solution, 0.1 per cent

0.375	9	28
0.383	18	27
0.387	29	19
0.397	43.5	26
0.399	64	25
0.413	84	30
0.440	104	21
0.427	126	15
0.294	148.5	15
0.442	171	14
—	177	—
0.361	203	9
0.348	231	—

(3) Potassium nitrate solution, 0.05 per cent

0.484	15	19
0.486	24	37
0.377	34	28
0.648	45	32
0.468	56	25
0.472	68.5	14
—	93	15
0.300	108	15
0.350	125.05	
0.356	141.5	27
0.374	175.5	15
0.345	204.5	17
0.273	234.5	8

TABLE IV

250 grams Elkton clay with 0.1525 gram $CaH_4(PO_4)_2$

Percolation rate cc. per min.	Total volume of percolate cc.	PO_4 in percolate p. p. m.
(1)	Distilled water[1]	
0.123	3.5	15
0.018	8.0	22
0.015	23.0	10
0.016	30.0	8
0.012	43	21
0.011	59	13
0.0095	76	12
0.0074	96	10
—[2]	110	6
—	129	8
0.0021	153.5	9
0.0022	182.5	5
(2)	Distilled water[3]	
—	0.5	—
0.038	4.0	—
0.050	59.0	13
0.066	70	10
0.063	87	5
0.059	148	5
0.032	197	7
0.032	241	6
—	256	8

[1] Soil was moistened and left over night before percolating at start of experiment.

[2] Started water through again. Clay remained wet on top and throughout its depth, but no water percolated after four days, when the water standing above soil was filled up to top of tube (2 inches) and in eight days more 19 cc had percolated. Steady percolation was maintained thereafter.

[3] 98.5 cc water was required to saturate 250 grams of soil, and required three hours to percolate to a depth of 12 cm, area of surface of soil being 16.7 sq. cm.

Sodium nitrate solution, 0.05 per cent

—	2	—
—	258	
0.023	264	7
0.026	292	
0.026	328.5	5
—	383.5	5
—	3	—
—	386.5	13
0.039	435.5	—
0.041	492.5	6
0.044	556.5	7

(3*a*) Distilled water

—	29.5	23
0.096	40.5	51
0.044	54.5	8
—	83.5	7
—	127.5	4
0.026	154.0	7
0.018	170.0	—
0.010	193.5	4
—	229.5	4
0.0076	246.5	9
—	275.5	6
—	294.0	6
—	329.5	15

(3*b*) Potassium nitrate solution, 0.05 per cent

start	3	—	
0.0105	13	342.5	8
0.0120	31	360.5	6
0.018	55.5	384.0	7
0.022	86.5	415.0	42
0.023	119.5	448	60
—	171.5	500	16
0.026	207.5	536	12
—	209.0	547.5	39

(3*c*) Potassium chloride solution, 0.05 per cent

Started again	22	569.5	lost
—	62	609.5	5
—	123	670.5	4
—	165	712.5	9

TABLE V

250 grams Elkton clay untreated

Percolation rate cc. per min.	Total volume of percolate cc.	PO_4 in percolate p. p. m.
	Distilled water	
	14	5
0.019	42	2
0.0115	54	19
—	63	13
—[1]	116	3
—	165	2

[1] The soil drained over night so that no standing water remained above it, consequently the rate of percolation is uncertain.

THE PERMEABILITY OF PORCELAIN AND COPPER FERROCYANIDE MEMBRANES

BY F. E. BARTELL

The relation between the diameter of the pores of membranes and osmotic effects obtained with the same membranes has been under investigation in this laboratory for several years by S. L. Bigelow[1] and co-workers. Experiments have been carried out with membranes of porcelain, collodion, gold beaters skin and parchment paper. Water was forced through these membranes and the permeability was determined under various conditions of temperature and pressure. It was found that Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through the above-mentioned membranes.

Values representing an approximation to the absolute permeabilities of these membranes were obtained. The permeability was expressed in terms of the number of cubic millimeters which pass through one square centimeter of membrane in one minute. This method of expressing permeability values was adopted in the present investigation.

Contents of this Investigation

Pressures used by Bigelow ranged between 9.8 mm and 834 mm of mercury. The work of Bigelow was repeated and verified, then extended through a much wider range of pressure. Pressures as high as 5885.7 mm of mercury were employed. The influence of temperature on the permeability of porcelain was also more fully investigated.

The permeability of copper ferrocyanide membranes, so much used in experimental studies of maximum osmotic pressures, was likewise determined. The permeability of these membranes, precipitated electrolytically in porcelain, was determined with temperature constant and with pressures varied between 58.6 mm and 2957.9 mm of mercury; also

[1] Jour. Am. Chem. Soc., 29, 1675 (1907).

with pressure constant and temperature varied between 20.5° and 65.5° C.

Apparatus

The apparatus used in the permeability determinations was a modification of that used by Bigelow and is illustrated in Fig. 1.

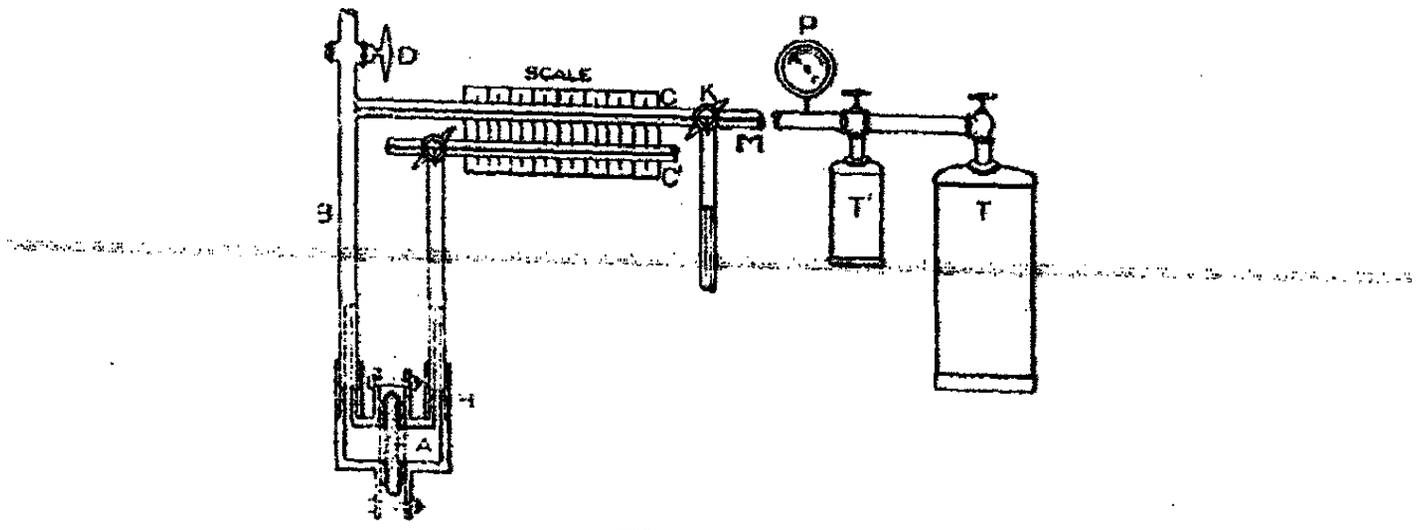

Fig. 1

The membrane which was to be studied, was placed between washers of rubber in the brass holder, H, which was tightened by means of three screws. The brass tube on one side of the holder was attached to a perpendicular glass tube, B, which was in turn sealed to the capillary tube C. This tube had been calibrated with mercury, and was used to measure the volume of water passing into the membrane. The brass tube on the other side of the holder was connected to the capillary tube C′, the outlet tube, which had also been calibrated with mercury. Tap D served to introduce the water to be used. Stopcock K served the double purpose of admitting air pressure to bear on the water column in C and of releasing the pressure at the close of the experiment. A small gas tank, T, such as is used for transporting oxygen, contained compressed air, and from this tank pressures could be applied as desired. Pressures were read directly from the pressure gauge, P. To diminish the decrease in pressure, due to the small change in volume, caused by the movement of the meniscus in the capillary tube, tank T′, was placed in con-

nection and served as an air chamber; with this arrangement there was no appreciable change in pressure during an experiment. When working with low pressures, the pressure tanks, T and T', were disconnected from the apparatus and in their stead mercury pressure bulbs were used. These bulbs were of good size, each having a capacity of about 250 cc. The lower bulb was attached directly to the air inlet tube, M. The other bulb, used to adjust the mercury pressure, was raised and lowered by means of a pulley and cord. A millimeter scale was placed in a perpendicular position between these bulbs, from this, readings were made by means of a cathetometer. The air space above the mercury, in the fixed bulb, was so large that the change of pressure during a single experiment was negligible.

Method of Measurement

The membrane holder was placed in water contained in a large beaker which was wrapped with layers of felt and asbestos. In this way the temperature was held constant, during an experiment, within half a degree. The tube B, was filled with distilled water by means of a capillary funnel, after which stopcock K was opened allowing the water to flow into the calibrated tube C. When the meniscus had reached the end of the scale, stopcocks D and K, were closed. The desired pressure was then applied, after which stopcock K was quickly opened allowing the pressure to bear on the water column. The water was forced through the membrane and out through the second capillary tube. By noting the distance over which the meniscus traveled in each tube along the millimeter scale, the volume of water passing into the membrane, and the volume coming through the membrane could be determined. By comparing these volumes it was possible to tell whether or not any leakage had occurred. The time for the meniscus to travel over a certain number of millimeters was noted by means of a stop watch. Usually the meniscus traveled over a distance of 50 mm. This represented a volume of 271.7 mm^3 (with the outlet tube this distance represented a volume

of 201.2 mm^3). The area of the membrane exposed was 1.767 cm^2.

Porcelain Membranes

Porcelain discs were cut from unglazed porcelain plates and ground, by means of emery paper, until they were about 4.5 mm in thickness and 30 mm in diameter. It was found that the amount of water which came through the membrane, and which was measured by means of the calibrated outlet tube, was considerably less than the amount forced into the membrane holder. This loss was due to leakage through pores which extended out to the edge of the porcelain disc. To diminish this leak the discs were coated with a layer of glaze[1] leaving uncovered only the central portion, about 15 mm in diameter.

Results with Porcelain

Temperature Constant, Pressure Varied.—Poiseuille's formula[2] for the passage of liquids through capillary tubes is: $Q = K \frac{P\ D^4}{L} T$. Q, represents the volume of liquid passing through a capillary tube of length L, in time, T. P, represents the pressure, D, the diameter, and K, represents a constant for a definite temperature.

According to this formula, the volume of liquid passing in unit time is directly proportional to the pressure.

Table I, contains results obtained by forcing water through porcelain at different pressures, the temperature remaining constant.

[1] A low melting glaze, consisting of PbO, 78 parts; $CaCO_3$, 10.3 parts; Al_2O_3, 7.1 parts; SiO_2, 42 parts, was used. A small amount of CoO was added to give it a color. The mixture was first fused, ground to a fine powder, then mixed thoroughly with glycerine. The glycerine mixture proved more satisfactory than the ordinary mixture of glazing material and water. The discs were heated in a muffle furnace until the glaze was thoroughly melted. They were then allowed to cool slowly. By this method a number of discs were prepared which were free from cracks, and which showed no measurable loss by leakage under the pressures used.

[2] Chwolson: "Lehrbuch der Physik.," Vol. I, p. 659 (1902).

TABLE I

Column I. Pressures in millimeters of mercury.
Column II. The number of cubic millimeters of water passing through the membrane (represented by A).
Column III. Time in seconds for the quantity, A, to pass through.
Column IV. Number of cubic millimeters which pass through one square centimeter of membrane in one minute (represented by Q).
Column V. Quotient obtained by dividing the Q values by the pressure, P.

I	II	III	IV	V
P	A	T	Q	$\frac{Q}{P}$
200	271.7	87.3	105.7	0.528
300	271.7	60.2	153.3	0.511
400	271.7	45.3	203.7	0.509
500	271.7	36.9	250.1	0.500
600	271.7	31.0	297.7	0.496
700	271.7	26.9	343.0	0.490

The temperature was maintained at 21.5° and did not vary more than 0.2° either way. The average thickness of the plate, measured by means of a micrometer caliper, was 3.84 mm, the thinnest portion 3.82 mm and the thickest 3.86 mm.

From the above results it is clear that the amount of water passing in unit time is very nearly proportional to the pressure. If the amount passing were exactly proportional to the pressure, the $\frac{Q}{P}$ values would be constant and this would mean that Poiseuille's formula for the passage of liquids through capillary tubes applies rigidly to the passage of water through porcelain. But these values, although nearly constant, do show a slight decrease with each successive determination.

To determine whether the decrease in permeability is merely a question of the time during which the experiment is running, of quantity of water passing through, perhaps of clogging of pores with solid particles, pressures were decreased in steps at definite time intervals and then, without stopping,

increased again through the same steps at the same time intervals. The results are given in Table II.

TABLE II

	P	A	T	Q	$\frac{Q}{P}$
1	400	201.2	60.4	113.2	0.2828
2	353	201.2	68.9	99.2	0.2809
3	297	201.2	83.2	82.1	0.2765
4	146	201.2	170.6	40.0	0.2745
5	53	201.2	474.0	14.4	0.2719
6	53	201.2	476.0	14.3	0.2708
7	146	201.2	173.6	39.4	0.2696
8	297	201.2	86.0	79.4	0.2674
9	353	201.2	73.8	92.5	0.2622
10	400	201.2	65.5	104.3	0.2608

Table III, contains the arithmetical mean of the two determinations at each pressure.

TABLE III

	P	A	T	Q	$\frac{Q}{P}$
1	53	201.2	475.0	14.35	0.2714
2	146	201.2	172.1	39.7	0.2720
3	297	201.2	84.6	80.7	0.2719
4	353	201.2	71.3	95.8	0.2714
5	400	201.2	62.9	108.7	0.2717

These results represent the mean permeability during an experiment and show an admirable constancy for the value of $\frac{Q}{P}$ *i. e.*, the amount passing is directly proportional to the pressure and Poiseuille's formula does apply.

The decrease in permeability must be attributed to one of two causes; either the porcelain undergoes some change in nature or the pores become clogged with insoluble material. By forcing water through the disc in the direction opposed to that in which it had passed during the experiment, and

brushing the surface with a fine stiff brush, the porcelain was put in such condition that it once more gave practically the same values as at the beginning. Freshly distilled water was used so that it hardly seemed possible that the clogging was due to impurities originally present in the water.

Bede[1] and Wilhelmy,[2] by different methods, arrived at the conclusion that the liquid layer in contact with a solid surface is less mobile than the remainder of the liquid. Duclaux[3] makes use of this conclusion and ascribes the decrease in permeability of membranes with continued passage of water, as due to the gradual thickening of the layer of the less mobile liquid on the walls of the capillary pores. The results of Bigelow's experiments show that the membranes of collodion and gold beaters skin do not show a similar decrease. This fact, together with the results mentioned above, makes Duclaux's theory improbable. Schmidt noted a change in permeability with continued passage of water through membranes. He ascribed a decrease in permeability to the clogging of the pores with solid particles. In his investigations he observed every precaution to remove impurities from the distilled water used. Quincke,[4] also obtained permeability results showing a decrease with continued passage of water. He was led to conclude that small particles were mechanically broken off the membrane and carried into the pores.

It seems that the most logical explanation of the decrease in permeability in the present investigation is that expressed by Quincke; *i. e.*, the gradual decrease in permeability of the porcelain membranes is due to clogging by small particles of porcelain which are mechanically broken off the plate and carried, by the water, into the capillary pores.

Since efforts to eliminate the trouble were unsuccessful the system of averaging, above described, was used in Tables

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[1] Bull. Acad. Belg., [2] 10, 47–55 (1860).
[2] Pogg. Ann., 122, 9 (1864).
[3] Ann. Chim. Phys., 25, 433–501 (1872).
[4] Pogg. Ann., 107, 21 (1859).

IV and V. In each of these tables temperature was held constant and pressures were varied.[1]

TABLE IV

P	A	T	Q	$\frac{Q}{P}$
76.7	40.24	160.1	8.53	0.1113
118.3	40.24	103.1	13.20	0.1120
228.7	40.24	53.8	25.40	0.1110
322.2	40.24	37.9	36.06	0.1119
405.3	40.24	30.1	45.39	0.1121
516.7	40.24	23.8	57.41	0.1111
622.9	40.24	19.7	69.36	0.1113
709.2	40.24	17.3	79.00	0.1114
827.8	40.24	14.9	91.70	0.1108
935.7	40.24	13.1	104.3	0.1115

Thickness of plate, 4.5 mm.
Temperature, 21.4°.

TABLE V

P	A	T	Q.	$\frac{Q}{P}$
1471.4	543.4	27.4	673.5	0.457
2207.1	543.4	18.4	1003.3	0.454
2942.8	543.4	14.0	1318.3	0.447
3678.6	543.4	11.3	1632.7	0.444
4414.2	543.4	9.3	1984.5	0.449
5150.0	543.4	7.9	2336.2	0.453
5885.7	543.4	6.9	2674.8	0.454

Thickness of plate, 4.5 mm.[2]
Temperature, 22°.

In the experiments with both low and high pressures, when corrections are made for the gradual decrease in permeability, we obtain, very nearly, a direct proportionality between the amount passing in unit time and the pressure.

[1] Pressures in Table IV were obtained with mercury pressure bulbs. Pressures in Table V were read directly from the pressure gauge and were converted to mercury pressures.

[2] The thickness of the plate was the same as in the previous experiment but the porcelain was of a different grade.

Pressure Constant, Temperature Varied.—In Poiseuille's formula $Q = \frac{KPD^4T}{L}$, K, represents a constant for a definite temperature. The formula to express the variation of K, with temperature is: $K = K_o (1 + 0.03368t + 0.000221t^2)$.[1]

In the present investigation, P and T (time) were held constant, and we will assume that D and L remain constant, we have then $\frac{PD^4T}{L}$ = a constant, C, which gives $Q = KC$. Substituting in the temperature equation we obtain

$$\frac{Q}{1 + 0.03368t + 0.000221t^2} = K_oC.$$

Having obtained the values for Q, T (time) and t (temperature) we can calculate the values for K_oC.

If Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through the membranes studied, we should get a constant value for K_oC.

Table VI, contains results obtained by forcing water through porcelain at constant pressure but at different temperatures.

TABLE VI

Column I. Pressures in millimeters of mercury.
Column II. Number of millimeters per minute meniscus traveled in calibrated tube.
Column III. Temperature.
Column IV. Number of cubic millimeters which pass through one square centimeter of membrane in one minute.
Column V. K_oC values.

P	mm. per min.	t	Q	K_oC
650	89.09	18	273.8	163.2
650	109.5	28	336.7	159.2
650	133.3	38	410.1	157.8
650	158.7	48	488.2	156.2
650	186.3	58	573.1	155.1
650	199.6	68	659.1	152.9
650	243.9	78	750.2	150.9

Thickness of plate, 3.94 mm.

[1] Chwolson: "Lehrbuch der Physik.," Vol. I, p. 659.

The values for K_oC should remain constant throughout the experiment for P and T were held constant in every case. The values are not constant; with each successive determination there is a slight decrease in the K_oC values which shows that there must be a smaller increase in the Q values with increase in temperature than should occur if Poiseuille's formula applies. These results are analogous to those obtained by Bigelow and are also similar to those obtained in Tables I and II. No allowance was made for clogging of pores.

Table VII, was obtained with still a different plate. Results at each pressure represent the average of six determinations. The system of averaging used in the pressure experiments, was employed.

TABLE VII

P	mm. per min.	ℓ	Q	K_oC
696.4	61.5	22.1	140.0	77.43
697.5	78.7	32.0	179.3	78.16
697.0	93.5	41.3	212.8	76.86
693.5	113.2	52.1	257.8	76.88
695.0	135.1	61.9	307.0	77.89
694.5	150.0	70.0	340.8	76.74

Thickness of plate, 4.5 mm.

The values for K_oC thus obtained show a fairly close agreement. When corrections are made for differences in pressure the values obtained are still more nearly constant as is noted in Table VIII. Q^p, represents the quantity which would have passed had the pressure been held constant at 693.5 mm. K_oC' represents the new values calculated from the Q^p values. These values are, in all probability, constant within the limits of experimental error.

TABLE VIII

t	P	P′	Q	Q^P	K_oC'
22.1	696.4	693.5	140.0	139.4	77.11
32.0	697.5	693.5	179.3	178.2	77.54
41.3	697.0	693.5	212.8	211.6	76.47
52.1	693.5	693.5	257.8	257.8	76.88
61.9	695.0	693.5	307.0	306.3	77.80
70.0	694.5	693.5	340.8	340.2	76.63

The change of permeability with change of temperature is in reality a measure of the change of the viscosity of the water due to this change in temperature. Poiseuille's viscosity formula is $\eta = \frac{\pi P R^4}{8QL} T^1$ (η represents the coefficient of viscosity). The pressure required to force a liquid through a capillary tube is directly proportional to the viscosity of the liquid, while the amount coming through, per unit of time, at any given pressure, is inversely proportional to the viscosity, *i. e.* $\eta'/\eta = Q/Q'$. Viscosity values calculated from the results in Table VIII, are given below in Column III of Table IX. These results were obtained by using the formula $\eta' = \frac{\eta Q}{Q'}$. As a basis for calculation, the values $\eta = 0.00957$ and $Q = 139.4$ were used.

An empirical formula for the calculation of viscosity at any temperature is: $\eta^t = \frac{\eta_0}{1 + at + bt^2}$. For water, $a = 0.0332$, $b = 0.000244$, and $\eta_0 = 1.775$.[2] Values representing the viscosity of water, at the temperatures employed in this experiment, were calculated by this formula and are given in Column IV.

[1] Chwolson: Vol. I, p. 643.
[2] Chwolson: Vol. I, p. 648.

TABLE IX

I t	II Q^v	III $\eta' = \frac{\eta Q}{Q'}$	IV $\eta' = \frac{\eta^\circ}{1 + at + bt^2}$
22.1	139.4	0.00957	0.00957
32.0	178.2	0.00747	0.00767
41.3	211.6	0.00630	0.00636
52.1	257.8	0.00518	0.00523
61.9	306.3	0.00436	0.00444
70.0	340.2	0.00392	0.00393

From these results it is apparent that a measurement of the change of permeability at different temperatures, pressure constant, is nothing more or less than a measure of the change of the viscosity of the liquid. It then follows, that if we know the amount of liquid which passes through a membrane in unit time, at a given temperature and pressure, we can readily calculate that amount which would pass through at any other temperature, $Q' = \frac{Q\eta}{\eta'}$.

Permeability of Copper Ferrocyanide

Pfeffer,[1] gives some permeability values obtained by forcing water through copper ferrocyanide membranes. He used pressures varying between 37.8 and 210.2 cm of mercury. His results are few and he gives only the pressures and the quotient obtained by dividing the amount of water passing through in unit time by the corresponding pressure. They indicate, however, a direct proportionality between the amount of water passing through in unit time and the pressure.

Sebor,[2] deposited a copper ferrocyanide membrane in a Pukall porcelain cup. He gives the results of one series of six observations, obtained at 18°, with pressures varying between 4 and 23.2 cm of water; the results obtained show a direct proportionality between the time and the pressure. He prepared a similar Pukall cell, precipitating the copper

[1] Osmotische Unterschungen, Leipzig, pp. 70–72 (1877).
[2] Zeit. Electrochemie, 10, 347–53 (1904).

ferrocyanide membrane by the electrolytic method of Morse.[1] By a test in which low pressures were used, he found that practically no water passed through the cell in 24 hours. No experiments were made with higher pressures.

Preparation of Copper Ferrocyanide Membranes

Copper ferrocyanide was precipitated, by the electrolytic method, within glazed porcelain discs similar to those used in the preceding experiments.

During the precipitation of the membrane, the plate A, was placed vertically between two glass cylinders, C and C′, each 40 mm in length and 30 mm in diameter with washers of rubber B and B′, between the ends of the cylinders and the porcelain. Into the other end of each cylinder was inserted a three-hole rubber stopper; in the upper holes were inlet tubes, D and D′, used for supplying the solutions; in the lower holes were placed the outlet tubes, F and F′, for the removal

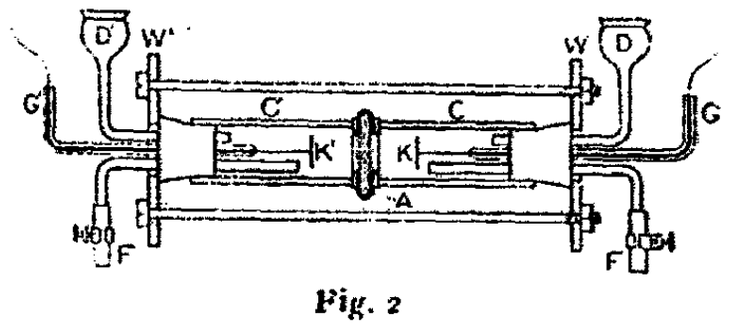

Fig. 2

of the alkaline solution formed during the precipitation; while through the remaining holes were inserted the connections carrying the electrodes K and K′, which were placed about 2.5 cm from the porcelain plate. Bearing on the ends of the rubber stoppers were two iron washers, W and W′, held by three screws with which pressure could be applied to keep the apparatus together.

The method for the removal of the air from the plate, as also the method for the deposition of the membrane, was practically the same as that used by Morse and Horn.[2]

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[1] Morse and Horn: Am. Chem. Jour., 26, 80–86 (1901).

[2] Loc. cit.

The precipitation was continued until a resistance of 400,000 ohms was obtained.

Results with Copper Ferrocyanide

The apparatus and method for the determination of the permeability of copper ferrocyanide membranes was the same as that used in the experiments with porcelain. The system of averaging results was not employed.

In the pressure experiments the temperature was maintained at 22° and did not vary more than 0.2° either way.

The values in Table X, were obtained with temperature constant and pressure varied.

TABLE X

P	A	T	Q	$\frac{Q}{P}$
588.5	54.35	720	2.56	0.00434
883.0	54.35	490	3.76	0.00426
1177.3	54.35	375	4.92	0.00417
1471.6	54.35	300	6.15	0.00418
1839.5	54.35	232	7.95	0.00439
2207.4	54.35	195	9.46	0.00428
2575.3	54.35	167	11.05	0.00429
2957.9	54.35	145	12.73	0.00430

The permeability values obtained with copper ferrocyanide are very much less than those obtained with porcelain but there is, however, the same direct proportionality between the amount of water passing and the pressure.

Table XI, contains results with pressure constant and temperature varied.

TABLE XI

P	mm. per min.	t	Q	K_0C
2207	6.74	65.5	20.73	4.938
2207	6.13	61.0	18.86	4.873
2207	5.40	53.0	16.62	4.885
2207	4.63	46.5	14.24	4.650
2207	2.86	20.5	8.79	4.935

In the experiments with both the porcelain and the copper ferrocyanide membranes values were obtained for $\frac{Q}{P}$ indicating that the amount of water passing was directly proportional to the pressure, also constant values were obtained for K_oC. It seems, therefore, that we are justified in concluding that *Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through porcelain and through copper ferrocyanide membranes.*

The fact that Poiseuille's laws apply to the passage of water through porcelain and copper ferrocyanide membranes is strong evidence in favor of the theory that these membranes are capillary in structure, though it is by no means conclusive proof of such structure. It is not difficult to conceive of a capillary structure in porcelain, but in the case of copper ferrocyanide the interstices are much smaller, they are in all probability within the region of molecular dimensions. These results, then, are in accordance with the conclusions reached by Bigelow from his work with collodion membranes, that "the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes." Furthermore, it seems improbable that we shall ever be able to differentiate, experimentally, between the region of so-called capillary spaces and the region of intramolecular spaces.

Summary of Results

In this investigation it is shown that the decrease in the permeability of porcelain, during the passage of water, is due to mechanical clogging of the pores. However, constant permeability values were obtained by employing a system of averaging results.

It is demonstrated experimentally that Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through unglazed porcelain from pressures of 53 mm of mercury to pressures of 5885.7 mm of mercury.

Poiseuille's formulation for the passage of liquids through

capillary tubes as influenced by change of temperature, is found to apply to the passage of water through porcelain from 22.8–70° C.

Poiseuille's laws, as expressing both pressure and temperature variations, were found to apply to the passage of water through electrolytically precipitated membranes of copper ferrocyanide in porcelain.

In conclusion, I desire to express my thanks to Professor S. L. Bigelow for the original suggestion and for his advice and interest throughout the work.

University of Michigan,
April, 1911

THE ELECTRICAL CONDUCTIVITY OF LIQUID SULPHUR DIOXIDE SOLUTIONS AT —33.5°, —20°, —10°, 0°, AND +10°[1]

BY EDWARD C. FRANKLIN

Introduction.—While engaged in studying the properties of liquid methylamine as an electrolytic solvent Franklin and Gibbs[2] noted the fact that the molecular conductivities of methylamine solutions in their dependence upon dilution exhibit a behavior strikingly different from that generally observed for solutions in other solvents. Instead of the usual continuous increase of the molecular conductivity with the dilution, they found that beginning with very concentrated solutions, the molecular conductivity rises with increasing dilution rapidly to a maximum, thence declines to a minimum, to be followed by a continuous rise, presumably to the final familiar maximum.

Following up the work of Franklin and Gibbs the writer returned to the study of the electrical conductivity of liquid ammonia solutions in order to determine whether any indications of a similar behavior on the part of concentrated ammonia solutions might be discovered. It was found[3] that although the phenomena observed by Franklin and Gibbs do not recur in the case of all liquid ammonia solutions, still the characteristic trend of the molecular conductivity curve was found to mark the behavior of certain salts in solution in this solvent.

With the object in view of determining whether the effect discovered by Gibbs is a general property of concentrated solutions, the plan was inaugurated of measuring the electrical conductivity of concentrated solutions in a number of electrolytic solvents. Sloan[4] has shown that concentrated

[1] Read before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Detroit meeting, June, 1909.

[2] Jour. Am. Chem. Soc., 29, 1389 (1907).

[3] Zeit. phys. Chem., 69, 272 (1909). (Arrhenius Jubelband)

[4] Jour. Am. Chem. Soc., 32, 946 (1910).

aqueous solutions of potassium iodide give indications of the Gibbs effect, and F. B. Beyer, working in this laboratory, has noted a similar behavior on the part of calcium ferrocyanide solutions. Other salts, however, fail to give any clear indications of the effect.

Certain results obtained by Walden and Centnerzwer[1] in their investigations on liquid sulfur dioxide as a solvent made it appear probable that a study of the electrical conductivity of concentrated solutions in this solvent would be productive of more positive results. The work described below will be found to justify this presumption. Furthermore, since it seemed possible that some relationships of value might be discovered by following the molecular conductivity of these solutions not only through varying concentrations at a given temperature but also at different temperatures, the plan of the work was extended to include measurements at as widely different temperatures as the apparatus in the form constructed would permit.

The Apparatus and Mode of Manipulation.—The apparatus used was in all essential respects the same as that described in a former paper,[2] excepting that the accessory cell A, shown in the figure accompanying the paper cited, was dispensed with and other minor changes were made which the requirement of conveniently and rapidly changing and adjusting the temperature of the thermostat rendered necessary. The procedure finally adopted for carrying on a series of measurements is as follows. By means of an arrangement of ingress and egress tubes, which suggests itself and therefore need not be described, a quantity of aqua ammonia is introduced into the Dewar tube thermostat P,[3] after which liquid ammonia is run into the thermostat bath until the temperature stands at —10°, the boiling point of the

[1] Bull. Acad. Imp. des Sciences de St. Pétersbourg, [5] 15, 17; Zeit. phys. Chem., 39, 513 (1902); and Zeit. anorg. Chem., 30, 145 (1902); cf. Franklin: Loc. cit.

[2] Zeit. phys. Chem., 69, 272 (1909).

[3] Loc. cit., p. 277.

solvent. The temperature regulating device is then set to maintain this temperature; the solution is made up and its conductivity measured; all after the manner described in the former paper. Aqua ammonia is then run into the thermostat until the temperature rises to 0°, when again the temperature regulating device is set to maintain this new temperature. As a result of the expansion of the solution in the conductivity cell its surface is now above the pointer J of the figure.[1] It therefore becomes necessary to adjust the surface again to the pointer which is accomplished by evaporating off a portion of the solvent by means of a current of hydrogen gas forced through the liquid in the manner previously described. After measuring the resistance of the solution the temperature is raised to + 10°, and the operations of adjusting the surface of the solution and reading the resistance is repeated. Then by means of air pressure on the surface of the bath liquid, the Dewar thermostat is emptied of its contents of aqua ammonia and liquid ammonia is introduced in its stead. The temperature regulator is then adjusted to maintain the temperature at —33.5°; sufficient sulfur dioxide is distilled into the conductivity cell to bring the surface of the solution to the pointer, when, after thorough stirring to insure homogeneity of the solution, a reading of the resistance is made. Aqua ammonia is again run in to the thermostat to bring the temperature, first to —20°, and then to —10°, thus completing a cycle of measurements at the chosen temperatures. A new dilution is then effected by running solvent into the cell and adjusting the surface of the solution to one of the upper glass pointers, when the cycle of measurements just described is repeated. After measurements have been made with the solution adjusted to the uppermost pointer a known portion of the solution is removed from the cell after the manner described in the paper cited, and the operations outlined above are repeated until the desired number of measurements has been made.

[1] Loc. cit.

The Solvent.—The solvent used was obtained by passing the gas from a cylinder of commercial liquid sulfur dioxide through a tube containing phosphorus pentoxide and condensing it in the accessory cell J, shown in the figures given in two previous papers.[1] Although no special precautions were taken to arrive at a solvent of the highest possible purity, it was nevertheless easy to obtain specimens showing a specific conductivity as low as 0.04×10^{-6} Kohlrausch units. Walden and Centnerzwer[2] give 0.09×10^{-6} as the specific conductivity of pure liquid sulfur dioxide.

The Conductivity Cells.—The cell No. 3, described in a previous paper[3] was used in making the measurements here given with the exception of those for ethylammonium bromide and dimethylammonium chloride. The measurements of the conductivity of these salts were made in a cell especially constructed for this work but which in use was found to be unsatisfactory. The results obtained for these two salts may be in error to the extent of several percent but are nevertheless recorded in order to show that the peculiar trend of the conductivity curves seems to be a general property of solutions in sulfur dioxide.

The resistance capacities of the cell No. 3 were checked at the conclusion of the measurements recorded in this paper and were found to be 3.107 and 0.0888 Kohlrausch units respectively for the high and low resistance pairs of electrodes at 20°. The volumes at —33.5° for the pointers J, 1, 2, and 3, respectively were found to be 16.75, 21.53, 25.97 and 33.13 cc.

Experimental Results.—Following are given in detail measurements of the electrical conductivities of a number of salts in solution in liquid sulfur dioxide through concentrations ranging from approximate saturation up to the highest dilutions which could be conveniently measured with any

[1] Jour. Am. Chem. Soc., 26, 503 (1904); and Am. Chem. Jour., 23, 279 (1900).

[2] *Loc. cit.*

[3] Zeit. phys. Chem., 69, 282 (1909).

degree of accuracy, and through a range of temperatures included between +10° and —33.5°. As was to be expected especial difficulties were encountered in working both at the highest and the lowest concentrations which render the results less accurate at these extremes. With the cell as constructed with three electrodes for measuring both good and poor conducting solutions it was found impossible to get good telephone minima when working with the most concentrated solutions for the reason that the resistance to be measured was too low. On the other hand, because of the elaborate precautions necessary for the measurement of the conductivities of very dilute solutions with any degree of accuracy, attempts were not made to obtain the final maximum values of the molecular conductivities of the salts studied. The observations on the solutions of potassium iodide and potassium bromide were carried to such dilutions only as were necessary to show the final order of the molecular conductivities for the chosen temperatures.

For some reason, which the writer is at a loss to explain, the results here given are not in close agreement with those of Dutoit and Gyr.[1] The discrepancy, which was not discovered until after the work here described was completed, led the writer to delay publication in the hope of repeating his measurements in order, if possible, to discover the cause of the discrepancy. However, opportunity of checking up this work has not presented itself, and since whatever value may be possessed by the work here given does not lie so much in the absolute accuracy of the data presented as in the general form of the curves and especially in the temperature effects observed, further delay in their publication seems unjustified.

In the tables below are given under the superscriptures $v/1000$, the dilution in liters per mol, and under —33.5°, —20°, —10°, 0° and +10°, the molecular conductivities in reciprocal ohms at the respective dilutions and temperatures. Following the direct experimental data given in these tables

[1] Jour. Chim. phys., 7, 189 (1909).

is for each salt a summary of the conductivity values interpolated for the dilutions indicated under $\varphi/1000$.

Potassium Iodide.—A specimen of J. T. Baker's "special" salt dried by gentle ignition was used. The two most concentrated solutions studied, containing respectively 55.5 and 41.3 grams of salt to 100 cc of the solution, deposited crystals of salt abundantly when cooled to —33°.

$\varphi/1000$	Λ				
	−33.5°	−20	−10	−0°	+10°
			I		
0.4470	24.80	—	35.87	—	—
0.5860	29.77	—	—	—	—
0.707	33.39	—	—	—	—
			II		
0.7892	34.70	—	—	—	—
1.008	37.47	—	—	—	—
1.601	39.74	—	—	—	—
			III		
0.2980	—	—	21.93	26.85	—
0.4702	—	32.57	37.81	42.60	—
0.6043	—	37.64	—	—	—
1.0882	—	44.16	—	—	—
			IV		
3.597	40.55	43.77	45.19	—	—
7.105	41.45	43.30	44.35	43.99	43.13
			V		
593.7	96.40	101.5	104.0	102.6	99.67
911.6	106.2	112.8	115.0	115.3	112.4
			VI		
604.7	96.70	102.8	103.9	—	—
			VII		
1.122	38.37	44.60	47.07	50.99	54.00
1.725	39.89	43.82	47.19	49.11	50.11
			VIII		
0.3543	—	23.88	29.39	34.82	40.44
0.5456	29.01	36.72	41.71	46.78	51.82

φ/1000	Λ				
	−33.5°	−20	−10°	0°	+10°
IX					
117.5	64.60	66.05	65.38	63.64	60.58
X					
59.72	54.40	55.39	54.82	53.32	51.02
91.82	60.34	61.46	61.04	59.01	56.62
XI					
55.66	53.99	54.74	53.98	52.10	49.71
110.5	63.43	—	64.25	—	—
217.9	—	—	77.63	—	—
431.1	—	—	94.70	—	—
XII					
72.07	—	—	57.25	—	—
110.8	—	—	64.83	—	—
218.9	—	—	78.18	—	—
433.8	—	—	95.03	—	—
858.2	—	—	114.3	—	—
1698.0	—	—	135.7	—	—
2184.0	126.0	134.7	144.1	146.3	144.7
XIII					
0.5848	—	—	42.28	—	—
0.7212	—	—	45.01	—	—
XIV					
47.89	—	—	52.05	—	—
73.65	—	—	57.29	—	—
145.4	—	—	68.95	—	—
287.3	—	—	83.78	—	—
567.5	—	—	101.7	—	—
1120.0	—	—	122.2	—	—
2214.0	—	—	144.4	—	—
4373.0	140.9	155.0	165.1	171.5	173.8
8638.0	—	—	190.7	—	—
XV					
5.406	—	—	43.50	—	—
6.945	40.42	42.24	42.66	42.50	41.77
10.68	41.37	42.64	42.73	42.14	40.88
21.09	44.30	45.35	44.84	43.69	42.06
41.66	—	—	50.27	—	—

XVI

φ/1000	−55°	50°	−41°	−33.5°	−10	0°	+10°	+33°
168.5	61.40	63.78	68.55	70.63	71.93	70.08	67.07	54.33

A

φ/1000	−33.5°	−20°	−10°	0°	+10°

XVII

446.9	—	—	95.94	—	—
686.8	—	—	108.0	—	—
1357.0	—	—	129.0	—	—
2680.0	—	—	147.4	—	—
5292.0	—	—	171.2	—	—

XVIII

479.4	—	—	98.20	—	—
947.0	—	—	117.9	—	—
1870.0	—	—	138.9	—	—
3694.0	—	—	161.2	—	—

XIX

434.7	—	—	04.48	—	—
858.6	—	—	113.4	—	—
1696.0	—	—	129.9	—	—
3355.0	—	—	158.2	—	—
6616.0	—	—	175.1	—	—
13070.0	—	—	192.2	—	—
16790.0	162.3	186.4	200.4	212.8	227.5

XX

1165.0	112.2	119.3	124.2	124.5	123.2
2300.0	128.2	137.0	145.2	147.3	148.1
4542.0	142.1	153.7	164.9	170.6	173.3
8972.0	155.8	171.0	185.5	194.3	201.5
17720.0	—	—	204.7	—	—

Summary of results for potassium iodide

φ/1000	A				
	−33.5°	−20°	−10°	0°	+10°
0.30	—	—	22.3	28.0	—
0.375	—	26.2	31.7	37.1	43.0
0.50	27.5	35.7	39.7	44.7	50.5
0.75	34.5	42.2	45.2	50.2	54.4
1.00	37.7	44.1	46.9	51.2	54.5
1.5	39.6	44.5	47.2	50.2	52.3
2.0	40.1	44.3	46.8	49.0	51.1
3.0	40.4	43.8	45.7	47.0	48.2
4.0	40.5	43.4	44.8	45.5	46.0
6.0	40.8	42.5	43.1	43.0	42.8
8.0	41.0	42.0	42.5	42.0	41.4
12.0	41.6	42.8	42.8	42.0	40.9
16.0	42.7	43.8	43.5	42.5	41.2
24.0	45.1	46.1	45.7	44.4	42.7
32.0	47.2	48.3	47.8	46.4	44.5
48.0	51.4	52.5	52.0	50.2	48.0
64.0	55.1	56.1	55.7	53.8	51.4
96.0	60.9	62.3	61.3	59.5	57.1
128.0	65.9	66.9	66.5	64.5	62.0
192.0	73.3	74.7	74.5	72.6	69.7
256.0	78.8	81.8	81.7	79.4	76.5
384.0	87.2	90.8	91.2	89.8	86.8
512.0	93.4	98.2	99.2	98.0	95.3
768.0	102.8	108.4	111.2	111.2	108.3
1000.0	108.6	115.2	118.8	119.4	117.7
1500.0	117.7	125.8	131.5	132.7	132.3
2000.0	124.2	133.0	140.5	142.3	142.3
3000.0	133.0	143.7	153.7	156.5	157.7
4000.0	139.0	151.0	162.5	166.3	168.7
6000.0	147.5	161.5	174.2	179.5	185.0
8000.0	153.0	168.5	181.8	189.0	196.0
12000.0	159.5	178.0	192.0	202.0	212.5
16000.0	163.0	184.0	199.0	211.0	223.0

Potassium Bromide.—The most concentrated solution measured contained 38.6 grams of potassium bromide to 100 cc of solution. The salt shows a negative solubility coefficient. From a 2.52 normal solution the salt crystallized out abundantly when the temperature was raised to 0°. Even a 0.42 normal solution deposited crystals when the temperature was raised to +10°.

φ/1000	A				
	−33.5°	−20°	−10°	0°	+10°
I					
51.13	—	—	37.57	—	—
101.0	—	—	45.54	—	—
II					
0.3961	21.25	28.42	32.78	—	—
0.6090	29.18	34.82	39.08	42.01	—
1.203	32.19	36.23	39.02	39.88	(38.95)
2.376	32.03	33.88	34.92	34.98	(34.23)
4.586	31.40	32.22	32.28	31.33	29.92
9.268	31.38	31.08	30.38	29.13	27.32
18.30	33.45	32.65	31.50	29.95	27.55
35.33	37.34	36.32	34.20	32.13	29.30
III					
41.35	38.47	37.55	35.51	33.64	30.73
81.68	46.11	44.84	42.40	40.25	37.08
161.3	55.89	55.00	52.85	49.87	45.83
318.7	68.58	67.27	65.88	63.06	57.95
629.3	84.06	84.08	82.74	79.04	73.23
1243.0	100.6	103.9	102.3	99.45	94.40
2456.0	118.7	122.8	125.3	123.8	118.0
4850.0	137.2	144.0	149.3	150.5	147.8

Summary of results for potassium bromide

φ/1000	Λ				
	−33·5°	−20°	−10°	0°	+10°
0.375	20.0	27.0	31.0	—	—
0.5	26.4	32.8	37.4	—	—
0.75	31.0	36.0	40.4	42.0	—
1.0	32.0	36.6	39.8	40.8	—
1.5	32.4	35.4	37.0	38.0	37.3
2.0	32.3	34.3	35.4	36.1	35.4
3.0	31.8	33.0	33.0	33.6	32.4
4.0	31.5	32.3	31.7	32.0	30.5
6.0	31.2	31.6	30.6	30.3	28.6
8.0	31.3	31.3	30.3	29.6	27.6
12.0	32.0	31.6	30.7	29.3	27.0
16.0	32.8	32.3	31.0	29.7	27.2
24.0	34.7	34.0	32.3	30.7	28.1
32.0	36.6	35.7	33.7	31.7	29.0
48.0	40.0	39.0	37.1	34.7	31.8
64.0	43.2	41.8	40.0	37.6	34.6
96.0	48.3	47.0	44.7	42.3	39.0
128.0	52.4	51.3	48.8	46.0	42.6
192.0	59.0	58.0	55.8	52.9	48.5
256.0	64.5	63.5	61.4	58.5	53.8
384.0	72.4	72.0	69.9	66.8	61.7
512.0	79.0	79.3	77.2	73.7	68.3
768.0	88.4	90.4	88.4	84.4	78.5
1000.0	94.7	97.7	96.0	92.5	86.7
1500.0	105.4	109.2	108.5	106.0	100.4
2000.0	113.3	117.4	118.0	116.2	110.3
3000.0	124.5	129.3	132.3	131.5	127.0
4000.0	132.0	138.0	142.3	142.5	139.3
4800.0	137.0	144.0	148.3	149.5	147.8

Tetramethylammonium Iodide.—The salt dissolves abundantly forming a yellow solution. The conspicuously high values for the molecular conductivity in the more concentrated solutions are noteworthy.

φ/1000	Λ				
	−33.5°	−20°	−10°	0°	+10°
		I			
8.35	74.50	80.90	86.94	90.12	93.06
16.49	77.70	84.20	89.58	92.30	94.98
32.58	83.24	88.04	94.78	97.12	99.50
		II			
34.18	—	—	94.78	—	—
67.52	89.68	96.38	103.2	105.9	108.2
133.3	100.4	107.5	115.7	119.5	122.7
263.3	107.4	—	127.1	132.0	137.2
		III			
0.3707	23.80	30.55	35.50	40.94	45.28
0.7322	54.54	61.29	68.00	72.80	80.64
1.446	67.83	76.22	84.42	89.60	95.58
2.857	73.82	81.94	88.60	93.52	98.12
5.641	75.83	83.36	89.92	92.86	96.64
11.15	—	—	90.32	—	—
22.01	—	—	93.46	—	—

Summary of results for tetramethylammonium iodide

φ/1000	Λ				
	−33.5°	−20°	−10°	0°	+10
0.375	25.0	31.5	37.8	41.6	46.5
0.5	40.3	45.7	52.5	56.7	63.3
0.75	55.3	62.3	69.4	74.0	81.7
1.0	61.3	69.4	77.0	82.2	89.0
1.5	68.3	76.6	84.8	90.0	95.8
2.0	71.2	79.7	87.5	92.7	98.0
3.0	74.0	82.0	89.3	93.5	98.3
4.0	75.0	82.8	89.5	93.5	97.5
6.0	75.5	83.0	89.5	92.3	95.7
8.0	76.0	83.0	88.5	91.3	94.3
12.0	76.7	83.4	88.5	91.3	94.3
16.0	77.6	84.0	89.3	92.0	94.7
24.0	80.0	86.0	91.7	94.6	97.3
32.0	82.0	87.5	94.2	96.7	99.5
48.0	85.5	92.0	98.5	101.6	104.0

64.0	88.6	95.5	102.3	105.0	107.5
96.0	94.4	101.7	108.7	111.8	115.4
128.0	98.5	106.6	113.5	118.0	121.5
192.0	105.0	114.0	121.3	125.4	129.5
256.0	109.5	119.3	126.7	132.0	136.5
384.0	115.7	126.6	135.0	141.0	146.5
512.0	120.0	132.0	142.2	148.5	154.5
768.0	125.5	139.3	151.5	158.7	166.8
1026.0	128.6	144.0	158.0	166.2	176.0

Ammonium Sulfocyanate.—The salt is extremely soluble; forming a yellow solution which, when concentrated, is very viscous. A solution containing 45.6 grams of salt to 100 cc of the solution is somewhat supersaturated at —10°. This solution, when cooled to —33°, changes to a solid mass of crystals.

φ/1000	Λ				
	—33.5°	—20°	—10°	0°	+10°
			I		
0.1664	—	—	7.30	9.37	11.51
0.2578	—	—	12.53	—	—
0.3287	9.70	11.93	13.81	15.37	16.69
0.6493	10.55	11.83	13.16	13.72	14.37
1.282	9.42	10.17	10.82	11.13	11.33
2.533	7.99	8.52	8.63	8.77	8.88
5.002	7.38	7.42	7.75	7.70	7.52
			II		
21.69	8.61	8.44	8.22	7.90	7.42
42.85	10.36	10.07	9.72	9.34	7.83
84.62	13.12	12.70	12.26	11.61	10.80
167.1	17.01	16.44	15.92	15.10	14.01
330.2	22.15	21.50	20.65	19.60	18.17
652.1	29.72	29.08	28.07	26.95	25.22
1288.0	39.55	38.77	37.55	35.78	33.84
2546.0	52.32	51.70	50.08	48.01	45.94
5024.0	67.48	67.22	66.69	63.81	60.81

Ethylammonium Bromide. Dimethylammonium Chloride.—As explained above the results for these two salts may be

in error to the extent of several percent. For this reason the original data are omitted and a summary only is given. When solvent was run into the most concentrated solution of dimethylammonium chloride it was observed to fall through the solution thus showing the solvent to be more dense than the solution, a rather exceptional relationship.

φ/1000	Λ for $C_2H_5NH_3Br$	Λ for $(CH_3)_2NH_2Cl$	φ/1000	Λ for $C_2H_5NH_3Br$	Λ for $(CH_3)_2NH_2Cl$
0.20	12.0	—	16.0	25.5	12.2
0.25	18.5	(14.3)	24.0	27.0	12.6
0.375	27.0	19.5	32.0	28.7	13.5
0.50	31.4	20.7	48.0	31.7	15.0
0.75	33.5	20.3	64.0	34.6	16.5
1.0	33.2	19.5	96.0	39.5	19.4
1.5	30.8	17.2	128.0	43.3	21.6
2.0	29.3	15.8	192.0	49.7	25.0
3.0	26.8	13.8	256.0	55.3	28.0
4.0	25.7	13.0	384.0	62.2	33.5
6.0	24.5	12.1	512.0	68.3	—
8.0	24.2	12.0	768.0	80.0	—
12.0	24.7	12.0	1000.0	88.0	—

Graphical Representation of the Results.—From an inspection of the experimental results of this investigation as summarized in the Figs. 1 and 2 in which the molecular conductivities are plotted as ordinates and the logarithms of the dilutions as abscissas, it will be obvious that the molecular conductivities of salts dissolved in liquid sulfur dioxide exhibit the same behavior as has already been recorded for solutions in methylamine and ammonia.[1] The molecular conductivity first rises to a maximum, then falls to a minimum, then again rising continuously to a final maximum at high

[1] Jour. Am. Chem. Soc., 29, 1389 (1907); Zeit. phys. Chem., 69, 272 (1909).

dilution. The effect of temperature changes on the trend of the molecular conductivity curves is also obvious.

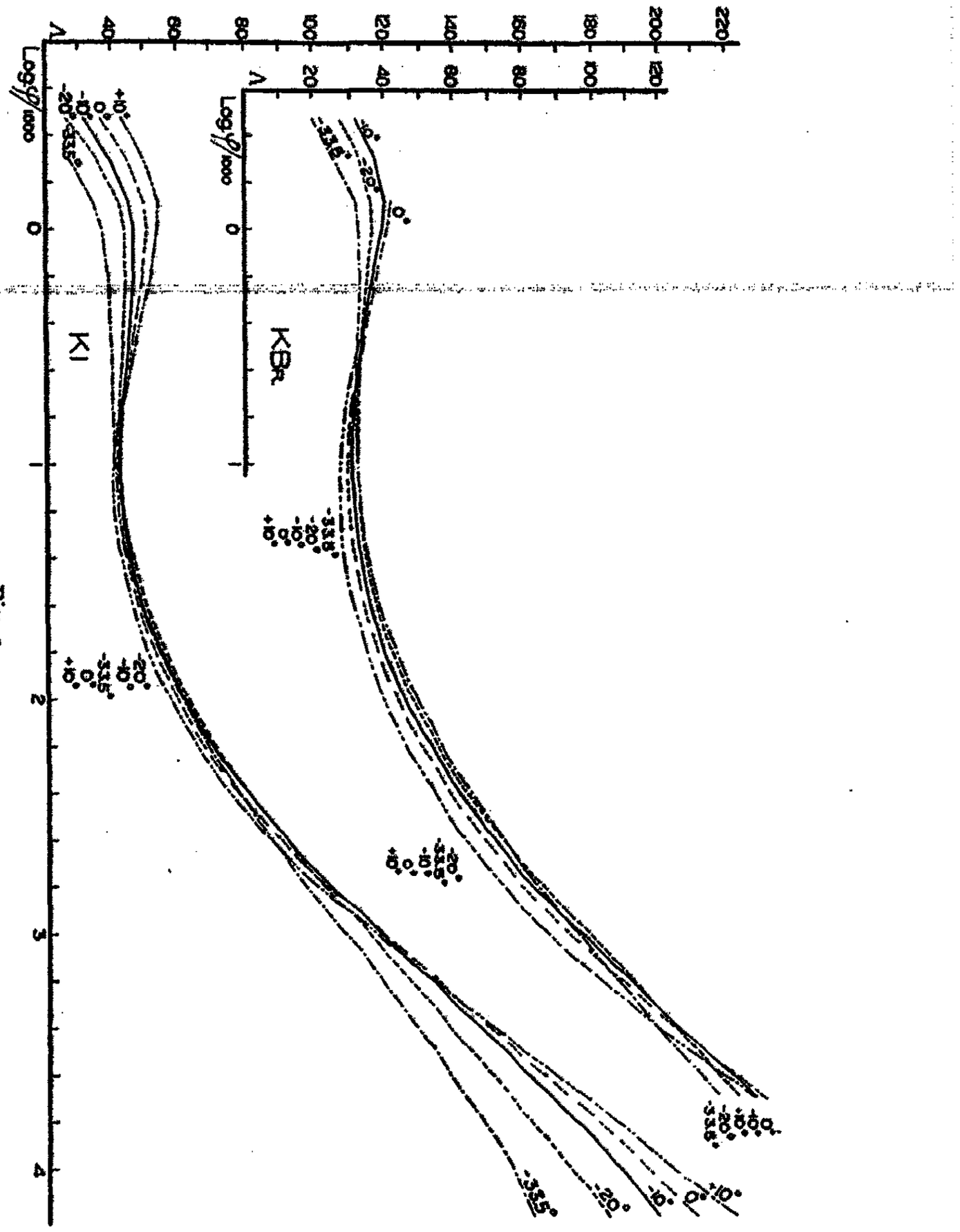

Fig. 1

Discussion of Results.—As an attempt at a tentative explanation of the phenomena recorded in the numerical data and curves herewith, the following considerations are submitted.

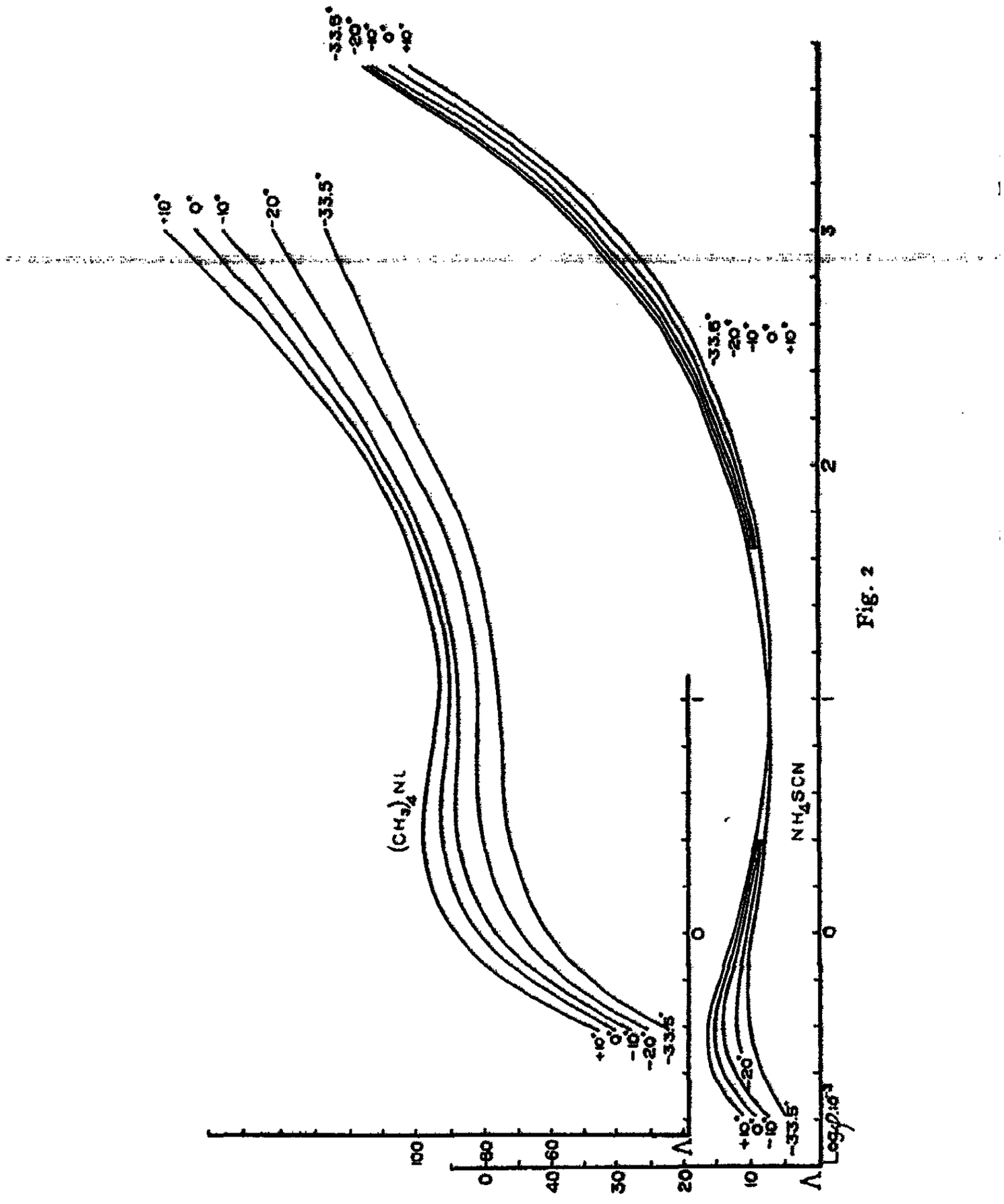

Fig. 2

In the first place such curves, or portions of them, have so far been observed only in connection with the weaker ionizing solvents such as the amines,[1] ammonia,[2] sulfur dioxide,[3] ether,[4] bromine,[5] iodine,[6] the halogen acids,[7] molten mercuric chloride,[8] molten boracic anhydride,[9] etc.,[10] that is to say, the effects, whatever the nature of their cause, which are superimposed upon the ordinary dissociating action of the solvent are conspicuous in solut ons in weak ionizing solvents, while in solutions in the more powerful ionizing solvents they are obscured.

In the second place, since the conductivity of melted salts is electrolytic and not metallic in its nature, it may be assumed as established that melted salts are ionized. Furthermore, the conclusion seems to be fairly well justified that in the melted state the observed conductivity is to be accounted for on the hypothesis of a high degree of ionization together with low ionic mobility.[11] It therefore seems reasonable to assume that in very concentrated solutions,—inasmuch as such solutions approximate the state of melted salts,—autoionization, or selfionization, of the solute plays a much more conspicuous part than in dilute solutions. If on this hypothesis we consider a very concentrated solution

[1] Franklin and Gibbs: Loc. cit.; Kahlenberg and Ruhoff: Jour. Phys. Chem., 7, 254 (1903).

[2] Franklin: Loc. cit.

[3] Walden and Centnerzwer: Loc. cit.

[4] Kablukoff: Zeit. phys. Chem., 4, 429 (1889); Euler: 28, 623 (1899); Sackur: Ber. chem. Ges. Berlin, 35, 1242 (1902).

[5] Plotnikoff: Zeit. phys. Chem., 48, 220 (1904).

[6] Lewis and Wheeler: Proc. Am. Acad., 41, 419.

[7] Archibald: Jour. Am. Chem. Soc., 29, 1416 (1907); Steele, McIntosh and Archibald: Phil. Trans. (A), 205, 99.

[8] Foote and Martin: Am. Chem. Jour., 41, 451 (1909).

[9] Arndt: Zeit. Elektrochem, 13, 405 (1907); Ber. chem. Ges. Berlin, 40, 2937 (1907).

[10] Walden: Zeit. phys. Chem., 43, 385 (1903); 54, 141 (1906). Coffetti: Gazz. chim. ital., 33, 63 (1902).

[11] Arndt: Zeit. Elektrochemie, 13, 509 (1907); Ber. chem. Ges. Berlin, 40, 2937, 3612 (1907). Lorenz: Ibid., 40, 3308, 4378 (1907); Zeit. anorg. Chem., 51, 71 (1906); 52, 41 (1907); Zeit. Elektrochemie, 10, 630 (1904).

of a salt in a non-ionizing, or very weak ionizing solvent, we may expect on diluting the solution, to find the autoionization, and with it the molecular conductivity, diminishing in value continuously with increasing dilution. The molecular conductivity of a salt dissolved in a non-ionizing solvent in its dependence upon dilution will then be represented by the curve C C′ C″ in[1] Fig. 3. The curve approaches

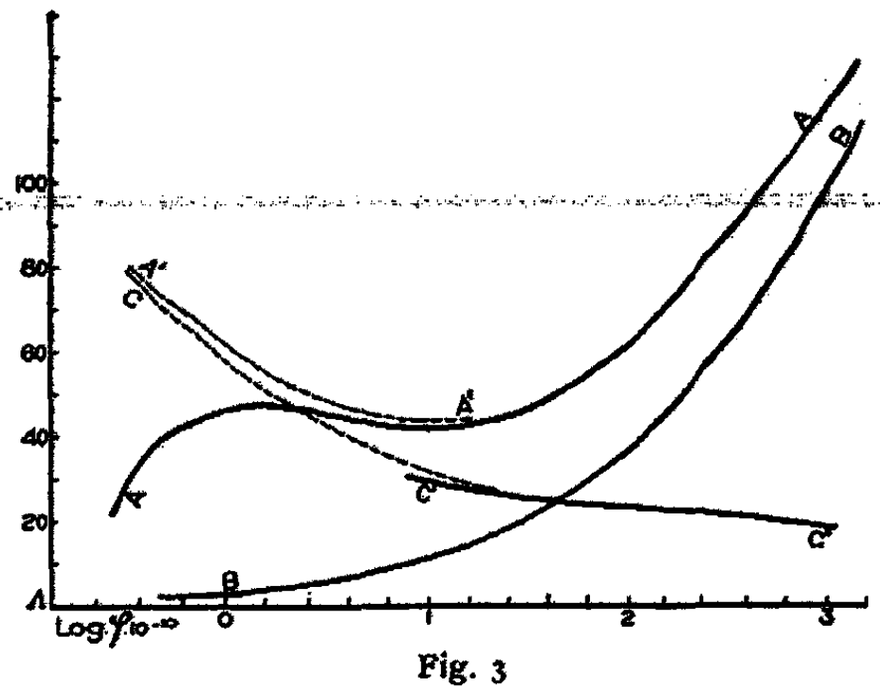

Fig. 3

the axis of dilutions asymptotically. Thus may be explained the downward trend of the molecular conductivity curve as recorded in this and previous papers.

In the third place, it is to be noted that while in concentrated solutions we have assumed the conductivity to be due in large measure, or even almost entirely, to the autoionization of the salt, in dilute solutions on the contrary, the ionizing effects must be ascribed to the solvent; for not only will the autoionization of the salt diminish with increasing dilution of the solution but also will the dissociating power of the solvent rise as a result of increasing solvent

[1] The points on the portion of the curve between C′ and C″ are plotted as the differences of the corresponding ordinates to the curves A and B, *i. e.*, the observed conductivity is the result of the superposition of the conductivity due to solvent ionization upon that due to autoionization. No data exist for the dotted portion of the curve, C C′.

concentration. In the ideal case in which the ionization in a solution is due wholly to the action of the solvent, and not at all to the action of the solute, the molecular conductivity curve must be that which is closely approximated by weak acids and bases in aqueous solutions. Such a curve, calculated on the assumption of a solution following Ostwald's dilution law, and with the assumed constants,[1] $\Lambda_\infty = 235$ and $\Lambda_\infty = (\Lambda_1^2\Lambda_2 V_2 - \Lambda_2^2\Lambda_1 V_1)/(\Lambda_1^2 V_2 - \Lambda_2^2 V_1)$ and $\alpha^2/(1-\alpha)V = K$. $k = 0.000298$, is Bβ in Fig. 3.

Now the two effects thus described are necessarily superimposed in the case of all actual solutions, with the result that at higher concentrations the one, at lower concentrations the other effect will have a preponderating influence on the trend of the conductivity curve. The molecular conductivity curve must therefore pass through a minimum as indicated in the figure. This minimum will show itself plainly and at no very great concentration in solutions in solvents of weak ionizing power, while in the case of solutions in powerful ionizing solvents the minimum will be pushed so far towards the region of greater concentration that it will be obscured, or be unrealizable because of the limited solubility of the solute, or because of the increasing viscosity of the solutions as explained hereafter.

Finally, it is an observed fact that concentrated solutions generally are more viscous, some of them much more viscous, than dilute solutions, from which it follows, when we remember that ionic mobility changes concomitantly with fluidity, that the observed conductivity must be much affected by the changing viscosity which accompanies dilution. The increase of fluidity of a solution with the dilution is represented by the curve D in Fig. 3, the location and trend of which however, are without quantitative significance.[2] Re-

[1] These constants are calculated from the conductivity data given above by means of the familiar formulas,

[2] Working in this laboratory F. F. Fitzgerald has shown a rapid rise in fluidity to accompany the dilution of concentrated solutions in liquid ammonia, liquid methylamine and liquid sulphur dioxide. The experimental results will be published.

calling the influence of changing dilution on the autoionization of the salt as explained above, it thus appears that there are two conflicting effects to be expected as the result of adding solvent to concentrated solutions; the one being a diminution in the degree of ionization of the solute, the other an increase in ionic mobility. The rapid initial rise in the molecular conductivity is due to the preponderating influence of the latter over the former on the current carrying capacity of the solution. These two effects must ultimately balance each other as the solution is diluted, and when they do, the molecular conductivity is at a maximum. As the solution is further diluted the effect of diminishing autoionization becomes predominant and the curve continues with a downward trend. As argued above the curve would continue to approach the axis of dilutions asymptotically in the case that the solvent possesses no ionizing power. Since, however, such in general is not the case we must expect sooner or later to find the downward trend of the curve arrested thence to rise, with continued dilution to the final familiar max mum as the result of the ionizing action of the solvent. The experimentally realized conductivity curve is that indicated in the figure by the lettering, A A. The dotted curve A″ A′ is drawn to represent the hypothetical trend of the molecular conductivity on the assumption of no change in the viscosity of the solution with increasing concentration.

Temperature Effects.—Having considered the influence of changing concentration on the conductivity of liquid sulfur dioxide solutions, as affected by the three factors, fluidity, autoionization and ionization due to solvent, we now turn to a very brief discussion of the influence of temperature changes on these factors.

The assumption has already been made that the conductivity of very concentrated solutions is due principally to autoionization of the solute. We may further assume that temperature changes are practically without effect on autoionization, for, if melted salts are highly ionized, then the liquefaction of a salt at a much lower temperature by the

action of a solvent cannot greatly alter this specific character of the salt.

Temperature changes are accompanied by changes in the viscosity of solut ons and these changes are especially conspicuous in the case of the most concentrated solutions. Specifically it has been shown in this laboratory that a rapid rise in the fluidity of concentrated solutions sulfur dioxide solutions accompanies rising temperature.[1]

The ionizing power of solvents generally diminishes with rising temperature.

Upon these temperature effects, of which the first only requires experimental substantiation, together with the effects of changing concentration as described above, are based the following qualitative explanations of the rather complicated trends of the molecular conductivity curves shown in the Figs. 1 and 2.

1. The conspicuous positive temperature coefficients of the most concentrated solutions are assumed to be due to the rapid rise in ion velocity which accompanies increasing fluidity; the degree of ionization at the same time undergoing negligible change.

2. Since rising temperature depresses the ionizing power of the solvent and is assumed to be without appreciable effect on the autoionization, the resultant effect of rising temperature must be to displace he minimum of molecular conductivity to higher dilutions and at the same to diminish its value. In accordance with this deduction the temperature coefficients of conductivity are seen to diminish in value as the solution is diluted to be followed by a complete change of sign in the case of solutions of ammonium sulfocyanate and potassium bromide. In the case of potassium iodide solutions the change of sign of the temperature coefficient extends only to the temperatures, $+10°$, $0°$, $-10°$ and $-20°$; the conductivity at $-33.5°$ never rising above that of

[1] Data by F. F. Fitzgerald. Not yet published.

—10° at any dilution. Furthermore the temperature coefficient of the molecular conductivity of tetramethylammonium iodide solutions remains positive throughout the whole range of temperatures and dilutions included in these measurements.

3. In very dilute solutions ionization approaches completion as the result of the dissociating action of the solvent. It follows therefore that in dilute solutions, even though rising temperature diminishes the ionizing power of the solvent, any change in the ionization of the solute must be subordinate in its effect on the conductivity of the solution as compared with the change in ionic mobility due to changes in viscosity of the solution with temperature. At sufficiently high dilutions, therefore the conductivity temperature coefficient must be positive. The curves show this to be true for solutions of potassium iodide and potassium bromide in liquid sulfur dioxide.

The writer is quite cognizant of the inadequacy and the too speculative nature of the above explanations, but presents them as the best he can do at the present time and in the belief that they are at least worth recording.

Summary

In this paper are recorded the results of measurements of the electrical conductivity of a number of salts in solution in liquid sulfur dioxide through concentrations varying from approximate saturation up to the highest dilutions which could conveniently be measured and through as wide a range of temperatures as could be readily realized with the apparatus in the form constructed.

It has been found that the molecular conductivity of liquid sulfur dioxide solutions instead of rising in the ordinary manner to a final maximum with increasing dilution, as a matter of fact rises first to a maximum, then falls to a minimum thence finally to rise to the familiar maximum at very high dilution.

Through the range of temperatures studied it has been found that the conductivity temperature coefficient is positive for very concentrated solutions and also for the most dilute solutions while for solutions of intermediate concentration the sign of the temperature coefficient is generally reversed.

A description of the method of manipulating solutions in liquid sulfur dioxide is given.

Stanford University, California,
May 1911

NEW BOOKS

An Introduction to the Chemistry of Paints. *By J. Newton Friend. 14 × 20 cm; pp. x + 204. New York: Longmans, Green & Company, 1910. Price: $1.20.*

In the introduction the author says: "This little work is the outcome of a series of lectures delivered to a class of Practical Painters and Decorators at the Darlington Technical College. The majority of the students could not be accused of possessing even a most elementary knowledge of chemistry, and further inquiries have shown that such is the condition of affairs among painters generally; although of course, there are notable exceptions, which serve to "prove the rule," as the saying is. The appreciation with which these lectures were received encouraged me to publish the same in book form, in the hope of appealing to a much larger circle, and of thus treating a wider interest in the subject.

"It is all very well to tell the youthful painter that cadmium yellow may not be tinted with white lead, and that it is unwise to mix together Prussian blue and lime; but he is very liable to forget such rules until he has learned their force by bitter experience. If, however, he is made to understand *why* these pigments are incompatibles, his interest is awakened, and the subject presents itself to him in an entirely new light. Now, this can only be done by a judicious inclusion of chemistry into the curriculum of the painter.

"But the very name of chemistry is enough to frighten many practical men, for the simple reason that the majority of chemists will persist in laying such stress on symbols and formulae, atoms and molecules. The consequence is that, before the student can begin to acquire a really practical and useful knowledge of chemistry, he has to wade through and memorize a number of (to him) dull and isolated facts, which might well be left out altogether, or at any rate reserved until the student has reached a more advanced stage. As the practical man has neither time nor inclination to do this, he not infrequently leaves chemistry severely alone, and therefore fails to appreciate its value and importance.

"It has been my endeavor, therefore, to show that a very thorough knowledge of the chemistry of paints may be acquired by the average student, without even a mention of such things as symbols, formulae, atomic weights, and the like; and for the sake of those who may wish to pursue any branch of the subject further, references are given, whenever possible, to more advanced literature and to original papers. Many recognized tests for pigments and liquid vehicles are included in the various chapters, and will, it is hoped, prove of service to manufacturers and color mixers. Should this work fall into the hands of the expert chemist, I trust that its pages will not be found altogether devoid of interest even for him."

The wish expressed in the last two lines is sure to be gratified. One especially interesting point is the use sometimes made of the fact that carbon black absorbs coloring matter, p. 54.

"You are all familiar with the trouble caused by the so-called 'bleeding

of the lakes.' In a later lecture I hope to explain to you how the lakes are prepared; I may so anticipate, however, as to say that they contain organic coloring matter, which has the awkward knack of bleeding through an indefinite number of coats of paint applied on top of it. This is practically troublesome if the upper surface of paint is to be white. I know of a case in which a painter coated some woodwork in a shop which had been previously painted with a carmine lake with eight coats of white, and still the red color bled through. What is the remedy? Many painters put a coat of knotting varnish over the lake, and then paint on top of that. Knotting varnish is simply ordinary shellac dissolved in methylated spirit. The spirit evaporates and leaves a thin coating of shellac behind, through which the coloring matter of the lake cannot pass. Unfortunately, however, this almost always cracks in drying, and the lake bleeds through the cracks. A very sure remedy is to make use of the property of the carbon blacks already referred to. Give the wood a good coating of a carbon black, and then you can safely paint on top of that. The obvious disadvantage is that, if a white color is required, an unusual number of coatings will have to be applied to completely block out the black. But the bleeding is stopped, and that is the main point."

The polymerization of tung oil by heat, p. 124, is distinctly an interesting phenomenon. The chapter on the lakes, p. 100, is a good one, though the reviewer doubts the statement that "theoretically, the amount of basic substance should be exactly sufficient to neutralize all the acid color—neither more nor less—to form a true lake."

The whole problem of driers for linseed oil, p. 151, is interesting to the chemist and the subject of varnishes, p. 179, is practically an untouched field.

Wilder D. Bancroft

Storage Battery Engineering. *By Lamar Lyndon. Third Edition. 17 × 25 cm; 601 pp. New York: McGraw-Hill Book Co., 1911. Price: $4.00.*

In the first part of the book the headings of the chapters are: Electrolytic dissociation and the voltaic couple; description and characteristics of the lead cell; chemical theory of the lead cell; thermodynamic theory of the lead cell; the quantity and distribution of active material; the electrolyte; electromotive force and its variation; capacity, internal discharge; the influence of temperature; efficiency; types of Planté plates; methods of Planté formation; pasted electrodes; applied active material mixtures; separators and envelopes; containing cells; testing; assembling and installing; durability and causes of deterioration; diseases and their remedies; care and management. The second part of the book is more especially of interest to the electrical engineer.

Take it all in all, the previous edition was the best book on the storage battery which we then had. For that reason the appearance of the third edition is very welcome. In most respects the new volume is an improvement on the old one. On the other hand, there is a distinct increase in the amount of theory included and some of this will not stand close inspection. On p. 4 is the statement that "the electromotive force produced by an electric battery is (strictly) proportional to the heat released by the chemical combination." The excess voltage does not depend, p. 13, on the ability of the electrodes to occlude hydrogen. The reviewer objects also to the following paragraph, p.

20. "Theoretically, if the elements only be considered, and the density of the electrolytes be maintained constant, the electromotive force of the cell should be constant up to the point of reduction to sulphate of the last traces of lead peroxide and lead, and then suddenly fall to zero. As a matter of fact, the voltage falls gradually from the beginning to end of discharge, and its failure to follow the above hypothesis has been the subject of no little speculation and research." There is no justification at all for the hypothetical lead oxides which are described on p. 27. *Wilder D. Bancroft*

Das chemische Gleichgewicht auf Grund mechanischer Vorstellungen. *By H. v. Jüptner. 16 × 24 cm; pp. 368. Leipzig und Berlin: Druck und Verlag von B. G. Teubner, 1910. Price: paper, 11 marks; bound, 12.50 marks.*

The author explains that a thermodynamic deduction involves the use of the term entropy and therefore he prefers to present the subject of chemical equilibrium from a purely mechanical point of view, meaning apparently from a kinetic point of view. The author shows a charming disregard for facts when he plots values for the dissociation pressures of $ZnCl_2.2NH_3$ and of $CdCl_2.6NH_3$ at 1300°, p. 117. He also plots, p. 127, the equilibrium pressures for $CaCl_2.6H_2O$, $CaCl_2.4H_2O$ and vapor up to 1300°. He seems to have obtained these remarkable results by extrapolating from Nernst's equations. *W. D. B.*

L'Essor de la Chimie appliquée. *By Albert Colson. 13 × 20 cm; 319 pp. Paris: Ernest Flammarion, Editeur, 1910. Price: 3 fr. 50.*

The first part of the book is really devoted to general and inorganic chemistry. The headings of the chapters are: historical sketch of chemistry; immediate applications, mechanism of reactions; chemical yields; heavy chemicals; agricultural chemistry; agricultural industries; the nitrogen cycle; chemical mechanics; osmosis; the beginning of electrochemistry; metallurgy; modifications and properties of the steels; lime and cements; inadequacy of chemical furnaces; cyanides and radioactive substances; the elements and their disintegration. The second part is devoted to organic chemistry and the headings of the chapters are: sugar, fats; cellulose; molecular constitution; tetravalence of carbon; physical isomerism; principles of hygiene; gas and tar; dyes; perfumes.
Wilder D. Bancroft

Gesammelte Abhandlungen. *By Friedrich Kohlrausch. Edited by W. Hallwachs, A. Heydweiller, K. Strecker and O. Wiener. Erster Band. 16 × 24 cm: pp. xxxv + 1108. Leipzig: Verlag von Johann Ambrosius Barth, 1910. Price: 25 marks.*—In view of what Kohlrausch has stood for and has accomplished in physics, the publication of his collected works will be welcomed by all interested in physics. This first volume contains the papers on elasticity, heat, optics and absolute electrical measurements together with some miscellaneous papers. The papers in this volume range in date of publication from 1863 to 1908, a period of forty-five years. Comment on the quality is unnecessary. The editors and the publishers are deserving of great credit for the speed with which this volume has been brought out. *Wilder D. Bancroft*

Die Grundlehren der höheren Mathematik. *By Georg Helm. 17 × 25 cm: 419 pp. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1910. Price: 13.40 marks; bound: 14.20 marks.*—This volume is based on the author's lectures to engineers, architects and chemists. Instead of separate courses in analytical geometry, in differential calculus, and in integral calculus, the three subjects are treated as one. Considered purely as an abstract proposition, there is a good deal to be said in favor of this way of treating the subject. Whether it is really better than the older way of doing things can only be determined by actual experiment. New ways of teaching subjects are always to be welcomed and this book can be recommended to those whose duty it is to struggle with these problems.

Wilder D. Bancroft

Themen der physikalischen Chemie. *By Emil Baur. 17 × 25 cm; 113 pp. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1910. Price: 4 marks.* —This is a course of lectures for engineers given during the summer holidays at Brunswick. The nine lectures are entitled respectively: physical chemistry; the voltaic cell; the blast furnace; heavy chemicals; catalysis; gas explosions; explosives; metallography; colloids and absorption.

Under the heading of the voltaic cell, the author discusses the lead storage battery, the Edison storage battery, and photo-cells. The chapter on the blast furnace is of course devoted to the equilibrium between iron, oxygen and carbon; it is distinctly an interesting presentation. In the fourth chapter the author discusses the manufacture of chlorine, sulphuric acid, nitric acid, and ammonia, pointing out that a knowledge of theoretical physical chemistry was not drawn upon at all in the working out of the Deacon process and was of relatively slight value in the development of the contact sulphuric acid process, whereas it has been of great importance in the work of preparing nitric acid and ammonia synthetically.

The chapter on catalysis has very little practical application as written and might perhaps have been omitted. The theoretical part of the chapter on gas explosions is interesting; but the author is evidently not familiar with the problems connected with the internal combustion motor, and he has consequently not made the most of his material. This lack of knowledge of the applied chemistry shows up again in the chapter on explosives which is rather a perfunctory one.

The chapter on metallography is better, though here one might make the criticism that the author does not point out how the composition of a phase is actually determined. The data on iron and steel are also neither the most recent nor the most accurate. In the chapter on colloids, the author begins by clearing up water with ferric hydroxide; then he dyes wool with methyl violet; and next he shows the movement of a drop of mercury in sulphuric acid when a crystal of potassium bichromate is added. With this as a beginning, the author discusses many of the theoretical problems connected with colloid chemistry.

One very good feature about the book is the number of lecture experiments which are described. These experiments must have added much to the impression produced by the lectures and probably helped the lecturer over some of the difficulties which are more noticeable when one reads the text. If the

author would take this same material and would work it up in a really thorough manner, he could write a very valuable book. *Wilder D. Bancroft*

The Simple Carbohydrates and the Glucosides. *By E. Frankland Armstrong. 15 × 24 cm; pp. vi + 112. New York: Longmans, Green & Co., 1910. Price: $1.20 net.*—In the preface the author says: "Twenty-eight years ago the late Sir John Burdon Sanderson described one of the aims of physiology as the acquirement of an exact knowledge of the chemical and physical processes of animal life. The recent history of biological progress shows that investigations confined to the study of physical and chemical processes have been the most fruitful source of physiological advance, and it is principally the exact chemical study of the substances found in animals and plants which has enabled the physiologist to make this advance."

The chapters are entitled: glucose, the chemical properties of glucose; the hexoses and pentoses; the disaccharides; the relation between configuration and properties; hydrolysis and synthesis; the natural and synthetical glucosides.

On p. 56 there is an interesting passage in regard to glucoronic acid. "Physiologically the most interesting product of glucose is glucoronic acid, which is frequently found in the urine combined with a variety of substances, forming compounds of glucosidic nature. It has not been identified as a plant product. Normally glucose is rapidly oxidized in the animal organism to carbon dioxide and water. When certain substances such as chloral or camphor which are oxidized in the body only with difficulty are brought into the system the organism has the power of combining them with glucose to form glucosides In such compounds one end of the glucose molecule is shielded from attack, but oxidation takes place at the other extremity of the molecule and a glucoronic acid derivative is formed. They are excreted in the urine. The faculty of removing injurious substances from circulation in combination with glucose seems to be common to both the animal and the vegetable kingdom, and the glucosides in the plant may be compared to the glucoronic acid derivatives in the animal."

How far we still are from any satisfactory theory of the plant syntheses may be seen from the following quotation, p. 71:

"It is now generally agreed that the protoplasm of the chlorophyll granule contains enzyme elements, and that it is these which occasion synthesis. The protoplasmic complex may be regarded as built up of a series of associated templates (enzymes) which serve as patterns for the maintenance of vital processes and of growth. The assimilated carbon dioxide, either before or after condensation to formaldehyde, is brought into contact with these templates in the protoplasm, and contiguous molecules are united to form the complete sugar, shaped according to the structure of the template. The enzyme specific for each particular hexose when incorporated in the protoplasmic complex may well serve as the template for its manufacture. Maltase, for example, should occasion the formation of α-glucose, emulsin that of β-glucose, lactase that of galactose, and invertase, or some similar enzyme, that of fructose. The existence of contiguous maltase and invertase branches in the protoplasmic complex might determine the formation of glucose and fructose in contiguity, and these might unite to cane sugar. Again two glucose molecules in contiguity

might unite to maltose, or a series formed in contiguity might remain potentially active so that a number would unite and give rise to a starch molecule. α- and β-glucose would remain as such as long as they were incorporated with protoplasm; when split off into the cell fluid they would no doubt tend to pass over into the equilibrated mixture."

On p. 75, we find the following paragraphs: "The manner of the synthesis by enzymes is still a matter of dispute. It is urged on the one hand that enzymes produce by synthesis the same bodies which they hydrolyze; on the other hand, it is suggested that the action of the enzyme is restricted to the formation of a compound isomeric with that normally hydrolyzed by the enzyme. A third view is that altogether distinct enzymes effect synthesis."

"Bayliss' contention that, if the synthetic body is incapable of being hydrolyzed by the enzymes present, action should continue until all the glucose is converted into disaccharide, does not sufficiently take into account the equilibrium resulting from the combination and sugar and the great retarding action of glucose—both thoroughly established facts. Further, each molecule of disaccharide formed liberates a molecule of water, thereby diluting the solution and lessening the opportunity for synthetic action. Lastly, enzyme extracts, unlike inorganic catalysts, do not remain of constant strength."

"The third view that synthesis and hydrolysis are effected by different enzymes, though not overlooked by earlier workers, has been brought into prominence by the recent experimental work of Rosenthaler. Emulsin in presence of hydrogen cyanide and benzaldehyde brings about the formation of optically active benzaldehyde cyanohydrin, a substance which it also hydrolyzes. Saturation of the enzyme solution with magnesium sulphate or half-saturation with ammonium sulphate produces a precipitate which is soluble in water. The filtrate has no synthetic activity, but is able to effect hydrolysis as before; the precipitate possesses synthetic activity and some hydrolytic activity. It is considered by Rosenthaler that emulsin consists of two distinct enzymes, one promoting synthesis, the other causing hydrolysis of benzaldehyde cyanohydrin."

If it should prove to be true that an enzyme can produce partial hydrolysis without having any synthetic power we should have a case of Duhem's false equilibrium.

"Opinions (p. 89) are divided as to the real significance of glucosides in plant economy. Probably they are of use to the plant in a variety of ways, and no one explanation will cover the functions of all the members of the group.

"In most, if not in all cases, the glucosides are accompanied by appropriate enzymes which are able to hydrolyze the glucoside. Enzyme and glucoside do not exist in the same cells as normally there is no decomposition. They are brought together should the cellular structure be damaged and in some instances during germination."

"In very many cases glucosides function as reserve materials and when required they are hydrolyzed by the accompanying ferment and pass into circulation."

"Anaesthetics such as chloroform or ether are well-known to have a remarkable action on plants in stimulating growth. A full explanation of this phenomenon is not yet forthcoming, though it has been supposed that enzymes

or similar agencies, hitherto dormant, are brought into activity by the action of the anaesthetic. Of the deepest significance in this connection is Grignard's observation that exposure of living plants to the action of the anaesthetics brings about interaction between the glucoside and the corresponding ferment. Mustard oil is formed from the leaves of certain cruciferae, hydrogen cyanide from laurel leaves and other cyanogenetic plants, when submitted to the action of chloroform. The same phenomenon is apparently brought about by exposure to cold produced by the evaporation of methyl chloride."

It seems to the reviewer that Hudson's work on the mutarotation of glucose deserves rather more recognition than the author has given it. *W. D. B.*

The Progress of Physics 1875-1908. *By Arthur Schuster. 15 × 23 cm; x + 146 pp. New York: G. P. Putnam's Sons, 1911. Price: $1.25.*—This is a most interesting book. The author gives a frankly subjective account of the development of physics during the last thirty-five years. Sometimes one agrees with the author and sometimes not; but in either case what he has to say is worth reading. On p. 3 we find that "the tendency to hide ignorance under the cover of a mathematical formula had already appeared but was not openly advocated; hence students were still taught to form definite pictures of the processes of nature."

On p. 7 the author quotes from a lecture delivered by Clerk Maxwell in 1871:

"This characteristic of modern experiments—that they consist principally of measurements—is so prominent, that the opinion seems to have got abroad, that in a few years all the great physical constants will have been approximately estimated, and that the only occupation which will then be left to men of science will be to carry on these measurements to another place of decimals.

"If this is really the state of things to which we are approaching, our laboratory may perhaps become celebrated as a place of conscientious labor and consummate skill, but it will be out of place in the university, and ought rather to be classed with the other great workshops of our country where equal ability is directed to more useful ends."

On p. 10, Schuster says:

"Altogether I am doubtful whether any great discovery has ever been made by anyone who has only aimed at recording a number of facts. I do not believe, in spite of what is sometimes asserted, that Schwabe was led to the discovery of the periodicity of sunspots simply by sitting down to record without ulterior motive the number of spots he could see; and it is to me unthinkable that the determination of the position of the planets, which allowed Kepler to discover his laws, was made by men who, solely for their own pleasure or satisfaction, recorded their places among the fixed stars. We may be certain that Schwabe had some idea on the possibility of connecting sunspots with other phenomena, and we know that the old astronomers were not doing their work simply for the sake of curiosity or in the vague hope that something unforeseen should come of it. Similarly we may be certain that Lord Rayleigh's object in determining the density of nitrogen, was not that of obtaining a more accurate value of physical quantity without some definite view, why an increased accuracy in the determination of that constant was desirable. The most important

result of a research no doubt is very often not that which was originally aimed at, but this does not prove the absence of an intention, which went beyond that of mere increased accuracy or an amplified record of facts."

The possibility of reading more into another man's writings than really was there is brought out clearly on p. 22.

"I formed some idea that if light is an electrodynamic disturbance, Weber's currents might be brought into connection with it and consequently tried a number of experiments (described in a note book which is still in my possession) on the influence of magnetism on the vibrations emitted by a sodium flame. All this was only vaguely before me, but I placed a sodium flame in the strongest magnetic field which the laboratory could provide and looked at the result through a spectroscope. To my delight, I found a widening of the lines. I sometimes wonder what would have been the result if I had then published what might now be considered as an anticipation of Zeeman's discovery; but as a matter of fact the effect was spurious and with the spectroscopic resolving powers used, I could not possibly have seen the real effect. After a few days of exciting work, I found indeed that the steel spring of the slit was drawn aside whenever the magnetic field was excited, and that the broadening of the line was simply due to the widening of the slit. By arranging the experiment differently, I could produce a narrowing of the line in place of the broadening. An experiment such as this ought to show the danger of taking it too easily for granted, that an observation recorded in some old book is an anticipation of a later discovery, when in reality it is probably only the result of a careless experiment accidentally simulating an effect which is real, but can only be detected by more refined methods."

There is a delightful passage on p. 48. "The man who looks upon his 'wire' as a common-place phenomenon, while he consider his 'marconigram' an almost super-natural message, is not very far removed in scientific education from the old woman who hung a pair of boots on the telegraph wires, so that they should reach her son more quickly than if they were sent by parcel post. An eminent man of science, to whom I once expressed my astonishment that wireless telegraphy was considered to be such a novel and extraordinary achievement, illustrated this general attitude by the remark that, if people had been accustomed to speak all their lives through speaking tubes they would be greatly surprised by the discovery that they also could speak without them. This puts the case exactly, the 'tubeless' speech is the accurate counter-part of the 'wireless' telegram."

In the discussion of conduction through gases, p. 52, there is a passage which must be quoted.

"The frame of mind with which the academic physicist looked upon investigations of the passage of electricity through gases, might be made the subject of instructive comment. The facts so far as they had been ascertained did not fit in with recognized views: hence they were ignored and students were warned off the subject. There was a feeling that perhaps in a century or so, the question might be attacked, but that in the meantime, it had better be left to be played with by cranks and visionaries. No criticism was more frequent at that time, than that of characterizing as premature any new idea or fresh line of investigation in this direction; as if any advance of science has ever been

made which was not premature a fortnight before it was made. It is perfectly true, and just as much the effect as the cause of the attitude assumed by academic science, that a vast quantity of time and labor had been spent on the subject without making any material advance. There were a great many pretty experiments which seemed to defy all rational explanations, and were too complicated to teach us anything very definite. If we look back upon these experiments now, they may be used to point the moral that experiments conducted in what is sometimes considered to be the true philosophic spirit, where the investigator without any preconceived theories or notions simply wishes to classify facts, seldom lead to any valuable results.

"Progress began when the subject was attacked with some definite object in view, either some theory however crude which had to be supported or some numerical connection which had to be investigated."

The last quotation is from p. 115. "To use an acute and celebrated expression of Gustav Kirchhoff, it is the object of science to *describe* natural phenomena, not to *explain* them. When we have expressed by an equation the correct relationship between different natural phenomena we have gone as far as we safely can, and if we go beyond we are entering on purely speculative ground. I have nothing to say against this as a philosophic doctrine, and I shall adopt it myself when lying on my deathbed, if I have then sufficient strength to philosophize on the limitations of our intellect. But while I accept the point of view as a correct deathbed doctrine, I believe it to be fatal to a healthy development of science. Granting the impossibility of penetrating beyond the most superficial layers of observed phenomena, I would put the distinction between the two attitudes of mind in this way: One glorifies our ignorance while the other accepts it as a regrettable necessity. The practical impediment to the progress of physics, of what may be reluctantly be admitted as correct metaphysics, is both real and substantial and might be illustrated from any recent volume of scientific periodicals. Everyone who has tried to add his mite to advancing knowledge must know that vagueness of ideas is his greatest stumbling-block. But this vagueness which used to be recognized as our great enemy is now being enshrined as an idol to be worshipped. We may never know what constitutes atoms or what is the real structure of the ether, why trouble therefore, it is said, to find out more about them. Is it not safer, on the contrary, to confine ourselves to a general talk on entropy, luminiferous vectors and undefined symbols expressing vaguely certain physical relationships? What really lies at the bottom of the great fascination which these new doctrines exert on the present generation is sheer cowardice: the fear of having its errors brought home to it. As one who believes that metaphysics is a study apart from physics, not to be mixed up with it, and who considers that the main object of the physicist is to add to our own knowledge, without troubling himself much as to how that knowledge may ultimately be interpreted, I must warn you against the temptation of sheltering yourself behind an illusive rampart to safety. We all prefer being right to being wrong, but it is better to be wrong than to be neither right nor wrong."

It is a pity that the author should have used the German spelling of the word, cathode, instead of the English one. *Wilder D. Bancroft*

Physical Optics. *By Robert W. Wood. 16 × 23 cm; xvi + 705 pp. New York: The Macmillan Company, 1911. Price: $5.25.*—The subject is treated under the following headings: the nature of light; rectilinear propagation of light; the reflection of light from plane and curved surfaces; refraction of light; dispersion; interference of light; the diffraction of light; interference of spectroscopes and the resolution of spectral lines; polarization of light; double refraction; circular and elliptical polarization; meteorological optics; theory of reflection and refraction; the theory of dispersion; absorption of light; optical properties of metals; rotary polarization; magneto-optics; electro-optics; fluorescence, phosphorescence, and resonance-radiation; laws of radiation; scattering of light by small particles; the nature of white light; the relative motion of ether and matter; the principle of relativity.

The author is known as an unusually skillful experimenter and special stress has been laid in this book on the experimental side. Among th interesting experiments described are: the subjective yellow, p. 10; the artificial mirage, p. 86; gelatine cylinders as pseudo-lenses, p. 87; the invisibility of glass in a mixture of chloral hydrate and glycerine, p. 99; the Christiansen effect with powdered quartz, p. 11; the flash spectrum of sodium, p. 116; the subjective yellow rings due to dissonance of lithium and thallium flames, p. 153; monochromatic light with potassium chlorate crystals, p. 161; the use of carborundum crystals for ruling grooves on copper, p. 228; production of supernumerary rainbows, p. 346; anomalous dispersion with a sodium vapor prism, p. 423; the selective reflection of mercury vapor, p. 429; the reversal of the red line in the hydrogen spectrum; p. 435; dichromatism of prism of brilliant-green and naphthalene-yellow, p. 439; fluorescence of sodium vapor, p. 576; luminescence of iodine vapor, p. 597; the lack of reflection by powdered marble, p. 632; the colors of granular films of gold, p. 637.

It is interesting to note the change of view in regard to the nature of white light, p. 648. "Previous to Newton's classic experiments on the decomposition of white light by a prism, it had been supposed that every refraction of light actually produced color, that is, the color was produced within the dispersing piece. Newton's experiments apparently showed, however, that the colors were actually present in the original light, the function of the prism being merely to separate them. At the present time, however, the view most generally held resembles in some respects the idea which prevailed previous to the time of Newton. Colored light implies a greater or less amount of regularity in the sequence of the waves. If a grating or prism yields us light which the eye is unable to distinguish from the light of the sodium flame, it is pretty certain that the luminous impulses are following one another at approximately the same intervals, as in the case of radiation from the sodium molecule. The question now is, were these regular wave-trains present originally in the white light, or have they been manufactured by the grating? If the former is true, how are we to regard a vibration which is made up of regular trains of waves, each however of a different wave length? Obviously the motion of the ether must be regarded as the resultant of all the component trains, and the regularity of sequence, as we usually understand it, would disappear wholly in wave-motion of this nature. If, however, the regular wave-trains, or colored rays, are manufactured by the prism, we very naturally ask whether Newton's discovery was really a discovery after all."

Wilder D. Bancroft

Applied Electrochemistry. *By M. deKay Thompson. 16 × 23 cm; xii + 329 pp. New York: The Macmillan Company, 1911. Price: $2.10 net.* The headings of the chapters are: coulometers or voltameters; electrochemical analysis; electroplating, electrotyping, and the production of metallic objects; electrolytic winning and refining of metals in aqueous solutions; electrolytic reduction and oxidation; electrolysis of alkali chlorides; the electrolysis of water; primary cells; the lead storage battery; the Edison storage battery; the electric furnace; products of the resistance and arc furnace; the electrochemistry of iron and steel; the fixation of atmospheric nitrogen; the production of ozone. The book is valuable in that it represents a serious attempt to write the kind of book that is needed. The reviewer believes that there is a good deal of unapplied theory in the book, especially in the chapter on the electrolysis of alkali chlorides. That, however, is a matter of opinion, and there are only too many precedents for the author's policy.

The real criticism to be made on the book is that it is not up-to-date. The author does not know that the silver belt cathode was given up at Perth Amboy years ago, p. 59, and he has apparently never heard of the American Smelting and Refining Company. His account of the electrolytic extraction of zinc, p. 47, is singularly misleading. The electrolytic precipitation of gold from a cyanide solution is being driven out by zinc precipitation; but even then it deserves more than a paragraph, p 65. When describing the Castner mercury cell, p. 107, no reference is made to the patents of Mauran. The author has evidently never read any of the aluminium litigation and he gets his information about the aluminium process, p. 231, very much at second hand. No one would guess that the potassium cuprocyanide bath, p. 36, is only used as a starting bath. So it goes throughout. The book is not reliable and it is not thorough enough to be satisfactory except an extremely elementary course is given.

Wilder D. Bancroft

Die Brown'sche Bewegung und die wahre Existenz der Moleküle. *By J. Perrin: Deutsch von J. Donau. 16 × 24 cm; pp. 84. Dresden: Theodor Steinkopff, 1910. Price: paper, 2.50 marks.*—In this little volume we have an admirable presentation of the facts in regard to the Brownian movements. The author makes out a very good case and the book can be recommended to everybody. The reviewer was especially interested in the experiments, p. 43, on the distribution of the particles of mastic under the influence of gravity. The one weak point in the treatment is the transition from an emulsion to a true solution. If the change is a continuous one, we are confronted by the problem why the solute does not coagulate under certain conditions. *Wilder D. Bancroft*

A CONTRIBUTION TO THE SUBJECT OF THE HYGROSCOPIC MOISTURE OF SOILS

BY CHAS. B. LIPMAN AND LESLIE T. SHARP

SOCIÉTÉ CHIMIQUE DE FRANCE BIBLIOTHÈQUE

In a recent publication of the Bureau of Soils, Patten and Gallagher[1] give experimental data in support of the principle enunciated by Knop and Schübler and adhered to by other investigators, that the power of soils to absorb hygroscopic moisture from a saturated atmosphere decreases with a rise in temperature and increases with a decline in temperature. The above-named investigators preface their work with a review of the more important investigations on the subject of hygroscopic moisture in soils and show that all but one investigator, Hilgard, have supported the results of Knop, as above stated. Hilgard, however, as they have pointed out, found in his investigations that not only does the power of soils to absorb hygroscopic moisture not decrease with a rise in temperature, but that it actually increases provided the atmosphere is *saturated*. It appeared to us, therefore, that it was highly desirable to prosecute further investigations not only relative to the temperature question, above referred to, but also to the methods involved in the study of the powers of soils to absorb hygroscopic moisture, as well as other phases of that subject. In order that the data on the effects of temperature might be established on a well justified method, the first experiments were carried out on the effects of the depth of the soil layer on the absorption of hygroscopic moisture from a saturated atmosphere.

Air-dried samples of a Berkeley clay adobe soil, from the campus of the University of California, were sifted through the 0.5 mm. sieve and distributed in duplicate in 1-gram, 3-gram and 6-gram portions in weighing bottles which were about $1^{3}/_{16}$ in. in diameter and $1^{15}/_{16}$ in. in height. They were arranged on a glass plate which was placed on a porcelain acid dish partly filled with distilled water and set in turn on a

[1] Bureau of Soils, Bulletin No. 51, U. S. D. A.

ground-glass plate, over the whole of which was fitted a bell jar of the short, squat form, to the inside upper portion of which was pasted a considerable quantity of thoroughly moistened filter paper. The ground rim of the bell jar was well covered with vaseline so as to permit of no escape of the moisture from the bell jar and thus insure a thoroughly saturated atmosphere. The apparatus was then placed on a shelf in a small room as far as possible from currents of air and where the temperature could be raised at will by lighting a Bunsen burner. A centigrade thermometer was placed next to the bell jar so that the temperature could be taken accurately just previous to removing the bottles from the jar for weighing. From the amounts of soil placed in the weighing bottles we had a depth in the case of the 1-gram samples of 1.5 mm, in that of the 3-gram samples of 4 mm and in that of the 6-gram samples of 8.5 mm. The covers of the weighing bottles were protected from moisture and dust under a separate bell jar and were so arranged on a glass plate as to allow of their being placed in their respective bottles in two or three seconds, from the time when the jar in which the samples were exposed was raised from the ground glass plate, thus preventing any loss of moisture. Table I gives the results of the weighings made through a period of 334¾ hours. The differences due to changes of temperature may be ignored here, since that matter is taken up in another series of experiments, the results of which are given below, but to which they lend further support. No further explanations of the technique and other details of the experiment need be given here since they are fully considered in the table.

The results in Table I bring out quite clearly the fact that anything but a very thin layer of soil cannot be used for the determination of the hygroscopic coefficients of soils, since even with as thin a layer of soil as 3 mm it was impossible to saturate it in less than three days and in the case of the 6 mm layer it was found impossible to saturate the soil until nearly the end of the experiment, or considerably over 400 hours. It must be said here also that the data given above as well as

TABLE I

Kind of soil	Depth of soil mm	Wt. of soil Gram	No. of hours exposure	1½	3½	24½	28¼	31½	70¾	77¾	94¾
			Temperature	18° C.	23.5° C.	23.5° C.	30° C.	34.75° C.	12° C.	25° C.	12.5° C.
Clay adobe	1.5	1	Av. gain in weight in grams	0.0060	0.0108	0.0203	0.0271	0.0320	0.0276	0.0373	0.0305
			Av. gain in percent	0.60	1.08	2.03	2.71	3.20	2.76	3.73	3.05
Clay adobe	4	3	Av. gain in weight in grams	0.0078	0.0148	0.0386	0.0476	0.5333	0.0585	0.0699	0.0649
			Av. gain in percent	0.28	0.49	1.28	1.58	1.77	1.95	2.33	2.16
Clay adobe	8.5	6	Av. gain in weight in grams	0.0086	0.0181	0.0582	0.0696	0.0783	0.0957	0.1078	0.1064
			Av. gain in percent	0.14	0.30	0.95	1.16	1.30	1.59	1.79	1.77

TABLE I—(*Continued*)

Kind of soil	Depth of soil mm	Wt. of soil Gram	No. of hours exposure	102¼	126	142¾	174¼	241½	318¼	407¼	455¼
			Temperature	34° C.	26.5° C.	12° C.	24° C.	15° C.	21.5° C.	12° C.	14.5° C.
Clay adobe	1.5	1	Av. gain in weight in grams	0.0464	0.0407	0.0324	0.0406	0.0381	0.0423	0.0340	0.0364
			Av. gain in percent	4.64	4.07	3.24	4.06	3.81	4.23	3.40	3.64
Clay adobe	4	3	Av. gain in weight in grams	0.0854	0.0803	0.0754	0.0870	0.0853	0.0962	0.0922	0.0971
			Av. gain in percent	2.86	2.68	2.51	2.90	2.87	3.20	3.07	3.23
Clay adobe	8.5	6	Av. gain in weight in grams	0.1308	0.1321	0.1285	0.1409	0.1438	0.1597	0.1659	0.1763
			Av. gain in percent	2.18	2.19	2.14	2.34	2.40	2.66	2.76	2.93

those given in the other tables represent averages of duplicate samples which throughout all the work agreed remarkably well, thus strengthening the accuracy of the work.

In view of the fact that most of the work thus far done on the hygroscopic coefficients of soils was done with thick and in many cases uneven layers of soil lends to the data above presented great significance and renders questionable some of the conclusions adduced from the other determinations. Indeed the depth of the soil layer employed seems to have been considered in the past by most investigators an insignificant factor despite the evidence which Hilgard, in work above referred to, has brought to light in that connection. Schübler and Knop have evidently not given the matter any consideration, and even in the very recent work of the Bureau of Soils above cited, 10-gram and 20-gram samples of soil were employed in weighing bottles, thus making a much thicker layer than the thickest employed by us in the experiment just described. In a short time, therefore, it is impossible to saturate a 10-gram sample of soil in a weighing bottle placed in a saturated atmosphere. It would appear from our experiments that even with a thin layer of soil of 1.5 mm at least 24 hours is necessary to saturate it in a weighing bottle. It is very probable though that in our regular method of determining the hygroscopic coefficients of soils the point of saturation can be reached in 8–10 hours for ordinary arable soils. This method is one devised by Hilgard and consists in sifting a quantity of the air-dried soil to be tested in a layer 1 mm thick on a piece of glazed paper which in turn is laid on a small wooden table with metal legs which stands in a box 12 × 18 × 19 inches high and made of boards $1^1/_2$ inches in thickness. The box and air-tight cover are lined with blotting paper which is thoroughly moistened and a layer of water at the bottom of the box about 1 inch in thickness is constantly maintained. The small tables upon which the soil samples are spread are so made that the tops are only about 1 inch above the surface of the water. This is absolutely necessary since it is difficult to obtain a saturated atmosphere

at any distance from the layer of water as Hilgard has found in his experiments on this subject. The box just described is kept in a cellar in which the temperature remains practically constant throughout the day and night. After an exposure of 8 hours the samples are quickly transferred to weighing bottles, the latter are stoppered and weighed. The stoppers are then removed, the bottles placed in an oven at 105–110° C and heated until the weight is constant. The percentage of hygroscopic moisture is thus calculated without any but small chances of loss.

The earlier determinations carried out by Mitscherlich, Knop and others in watch glasses with uneven depths of soil cannot have given correct results, especially since not only the depth of soil interfered but also the lack of a saturated atmosphere. It should be noted here also that there is a constant rise in the amount of moisture absorbed by the thicker layer of soil regardless of the temperature conditions until the point of saturation is reached.

Having thus again justified the method which could be relied on for the most accurate results, it was thought desirable to study the effects of temperature on the hygroscopic powers of soils in saturated atmospheres, and since the apparatus used by Hilgard and described above could not be conveniently placed under different temperature conditions during the course of the experiment the work was conducted in a bell jar as was the preceding series and the layers of soil used in the weighing bottles were made as nearly as possible 1 mm in depth. Three different soils, one of a low, another of a medium, and a third of a high, hygroscopic power were chosen for the work. The first was a light sandy soil from Anaheim, California, the second a clay adobe soil from the campus of the University of California, and the third was a tule soil with a high humus content from Klamath Lake, Oregon. All precautions employed with reference to the technique of the work in the preceding experiment were observed here The results follow:

TABLE II

Kind of soil	Depth of soil mm	Wt. of soil Gram	No. of hours exposure / Temperature	6 / 22.5° C	20½ / 15° C	29½ / 26.5° C	44½ / 16.5° C	53¾ / 29° C	71 / 14° C	77¾ / 25.5° C
Clay adobe	1.5	1	Av. gain in weight in grams	0.0160	0.0188	0.0278	0.0264	0.0378	0.0325	0.0374
			Av. gain in percent	1.60	1.88	2.78	2.64	3.78	3.25	3.74
Klamath Lake tule	2	1	Av. gain in weight in grams	0.0280	0.0429	0.0618	0.0654	0.0851	0.0854	0.0946
			Av. gain in percent	2.80	4.29	6.18	6.54	8.51	8.54	9.46
Anaheim sandy	1	1	Av. gain in weight in grams	0.0144	0.0129	0.0270	0.0186	0.0363	0.0253	0.0336
			Av. gain in percent	1.44	1.29	2.70	1.86	3.63	2.53	3.36

TABLE II—(*Continued*)

Kind of soil	Depth of soil mm	Wt. of soil Gram	No. hrs. exposure / Temperature	93½ / 17° C	100½ / 21° C	116¾ / 16° C	173 / 21° C	260¾ / 13° C	292½ / 20.5° C	332¾ / 13.5° C	334¾ / 21° C
Clay adobe	1.5	1	Av. gain in weight in grams	0.0340	0.0343	0.0346	0.0373	0.0301	0.0366	0.0346	0.0433
			Av. gain in percent	3.40	3.43	3.46	3.73	3.01	3.66	3.46	4.33
Klamath Lake tule	2	1	Av. gain in weight in grams	0.0928	0.0964	0.0969	0.1099	0.1133	0.1240	0.1234	0.1318
			Av. gain in percent	9.28	9.64	9.69	10.99	11.33	12.40	12.34	13.18
Anaheim sandy	1	1	Av. gain in weight in grams	0.0266	0.0281	0.0251	0.0350	0.0399	0.0433	0.0445	0.0487
			Av. gain in percent	2.66	2.81	2.51	3.50	3.99	4.33	4.45	4.87

The results in Table II would seem to give an unequivocal reply to the question of the effects of temperature on the hygroscopicity of soils. It would appear that as soon as the soil is saturated we have a rise of temperature accompanied by an increased absorption of hygroscopic moisture, and a fall in temperature accompanied by a loss of moisture from the soil. With the exception of the results of one or two weighings of the Anaheim soil towards the end of the experiment we find the results are so clearly in favor of the temperature effects just enunciated that no better evidence could be desired, to establish them.

We have here, therefore, data which confirm the results of Hilgard[1] and so far as we are aware the only data which agree with those of that investigator. In addition to the results of Knop and Schübler opposed to those of Hilgard, we have the exhaustive investigations of Schlösing,[2] and also the work of Ammon,[3] von Dobeneck[4] and others who worked with the various soil constituents instead of with soil. The objection to their methods must be urged however that they, as well as Patten and Gallagher, whose recent work is above cited, worked either with thick or with uneven layers of soil, or with both uneven and thick layers of soil, even though it be admitted that in some cases a saturated atmosphere was insured in the experiments. We are emphasizing the importance of the saturated atmosphere advisedly for in our own experiments, it has been noted on several occasions that when there was a condensation of vapor on the walls of the glass bell jar which trickled down to the ground glass and was allowed to remain there during one or two removals and replacements of the bell jar, that several places on the rim of the bell jar would be found free from vaseline and perfectly dry thus allowing an escape of vapor from the jar and undersaturation of the atmosphere within it. These occurrences

[1] Wollny's Forsch. a. d. Gebiete der Agrikulturphysik., 8, 93.
[2] Ibid., 7, 322.
[3] Ibid., 2, 1.
[4] Ibid., 15, 163.

were invariably accompanied by losses of moisture from the soils tested regardless of the temperature variations which had occurred during the period of exposure. Moreover, Hilgard has found in some more direct experiments, which remain as yet unpublished, but which were communicated verbally to one of us, that when the determinations were carried out in a tall bell jar with no saturated blotting paper in the upper portion of it, the soil samples placed at different heights from the water at the bottom of the jar showed different powers of absorption and namely those nearest to the water absorbed the most and those furthest from the water the least hygroscopic moisture.

It must also be stated here that our results do not show any increase in moisture absorption according to any geometrical or arithmetical ratio. Hilgard[1] has claimed that so far from following Knop's law of a steady decrease of moisture absorption with a rise in temperature according to a geometrical ratio, his experiments show an increase of moisture absorption, provided there is a saturated atmosphere, with a rise in temperature according to an arithmetical ratio. It is interesting to note here also that Hilgard adds, that in an *undersaturated* atmosphere, he was able to duplicate Knop's results and obtained a decrease in moisture absorption with a rise in temperature, according to Knop's geometrical ratio.

The next series of experiments was carried out to note the changes, if any, taking place in the hygroscopic coefficients of the same soils[2] used in the preceding series when the bell jar was placed in the incubator instead of in a room, under changes of temperature, produced by adjustments of the thermostat. The technique employed was the same as that described above. Table III shows the results of the experiment.

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[1] "Soils," Macmillan Co., 1903, p. 198.

[2] Owing to the breaking of one of the bottles containing the Anaheim soil, the latter is left out of consideration here.

TABLE III

Kind of soil	Depth of soil mm	Wt. of soil Gram	No. of hours exposure / Temperature	7 / 29° C	20 / 25.5° C	28 / 30.5° C	42 / 25.5° C	50 / 30.5° C	64 / 26.5° C
Clay adobe	1.5	1	Av. gain in weight in grams	0.0188	0.0170	0.0189	0.0170	0.0184	0.0175
			Av. gain in percent	1.88	1.70	1.89	1.70	1.84	1.75
Klamath Lake tule	2	1	Av. gain in weight in grams	0.0880	0.0836	0.0864	0.0828	0.0856	0.0834
			Av. gain in percent	8.80	8.36	8.64	8.28	8.56	8.34

TABLE III—(*Continued*)

Kind of soil	Depth of soil mm	Wt. of soil Gram	No. of hours exposure / Temperature	72 / 30° C	86 / 23.5° C	94 / 28° C	132 / 26° C	139 / 30° C	177 / 25.5° C	185 / 30.5° C	200 / 27.5° C
Clay adobe	1.5	1	Av. gain in weight in grams	0.0184	0.0169	0.0210	0.0161	0.0171	0.0169	0.0197	0.0171
			Av. gain in percent	1.84	1.69	2.10	1.61	1.71	1.69	1.97	1.71
Klamath Lake tule	2	1	Av. gain in weight in grams	0.0854	0.0814	0.0888	0.0821	0.0836	0.0836	0.0883	0.0835
			Av. gain in percent	8.54	8.14	8.88	8.21	8.36	8.36	8.83	8.35

In the table above given we find further confirmation, under incubator conditions, of the effects of temperature on the hygroscopicity of soils already noted in the preceding experiments. During a period of 9 days in the incubator, we find the soils to absorb more hygroscopic moisture with a rise in temperature and less with a fall in temperature. Here again by using the incubator, as did Patten and Gallagher, we obtain results that are the very reverse of their results.

An interesting difference between the moisture absorptions taking place when the bell jar is in the incubator and those taking place when it is in the room, may be observed from a comparison of Tables II and III. We are here confronted with a case of the absorptions taking place according to the same law in both experiments, namely, rising and falling with the temperature and yet the total capacity for holding hygroscopic moisture by the same soil in the incubator is considerably lower than it is in the room, the atmosphere being saturated in both cases. This is a striking phenomenon which we are at a loss to explain and for which indeed we have been unable to obtain an explanation from physicists and physical chemists to whom we have appealed. We trust that this problem will, however, find solution in the near future.

While thus the results obtained by the writers constitute a confirmation of the data obtained by Hilgard and while in our opinion there cannot be any other effects of temperature on the hygroscopicity of soils except as above enunciated, we cannot confirm any statement of a law for the increase in moisture absorption by a soil according to any arithmetical or geometrical ratio. At least the data adduced in our experiments do not justify the formulation of any such law. It will be found on an examination of the data above presented that in some cases the same amounts of moisture are not held by a given soil at the same temperature on two different days, especially when the temperature had been raised to 34° or 35° C from room temperature and then again cooled down to something near the room temperature. This can

undoubtedly be explained by the deposition of dew, owing to the sudden lowering of the temperature in the latter case and the subsequent lack of time, before weighing, for the saturated atmosphere of the soil and air to come to equilibrium as a result of which the soil holds more water after sudden cooling from a high temperature to the room temperature than it did at the latter before the temperature was raised.

General Remarks and Practical Considerations

It seems quite incomprehensible to us that data such as those obtained by other investigators with the exception of Hilgard could have been found in saturated atmospheres, for in our experiments it was only under conditions where the atmosphere was manifestly undersaturated that soils displayed any tendency toward a loss of hygroscopic moisture with a rise in temperature. There must be mentioned here in further support of Hilgard's results and our own the work of Van Bemmelen[1] which, while carried out along different lines, brought to light the fact that the absorption of moisture by gelatinous hydrates increases with the vapor pressure. That being the case it appears clear that in a saturated atmosphere, a rise in temperature would be accompanied by a larger amount of vapor and hence of a greater vapor pressure and a greater moisture absorption.

We feel constrained to emphasize again the importance of the effect of the depth of the soil layer on the accuracy of the determination of the hygroscopic coefficients of soils. It is manifest from our experiments that only a very thin layer of soil can be saturated in a short time, and the latter consideration is important because it excludes the inevitable errors which must enter into such determinations through the deposition of dew during long exposure of the soil. We, therefore, must strongly urge the adoption of the Hilgard method for the determination of the hygroscopic powers of soils above described. We are now contemplating further experiments with the Hilgard method, looking toward the

[1] Zeit. anorg. Chemie, 5, 467, and literature there cited.

determination of the number of hours necessary for the determinations of the hygroscopic coefficients of various types of soils.

As to the practical significance of the hygroscopic moisture of soils we need add but little to the very thorough investigations of Sachs and the criticisms thereof by Heinrich, Lieberg and Mayer, based on elaborate experiments which are familiar to all engaged in investigations on soils. To these have also been added the observations of Hilgard[1] which point to the fact that hygroscopic moisture is neither sufficient for supplying plants with moisture as claimed by Sachs and others, nor is it to be considered as of no significance at all for plants as claimed by Mayer, but is to be looked upon as a protective agent for plants from the scorching effects of the hot, dry winds which, were it not for hygroscopic moisture and the cooling effects due to its evaporation by them, would cause the wilting and destruction of plants. From the data adduced by us it is plain that plants, especially those of the arid regions, would find great protection from the large amounts of hygroscopic moisture absorbed by soils with rising temperatures.[2]

We cannot agree further with Patten and Gallagher that equilibrium conditions are seldom found in the field, for the frequent and heavy fogs which occur so constantly in many climates are without doubt accompanied by equilibrium conditions and allow of the absorption of hygroscopic moisture as indicated by us. Moreover, field conditions cannot enter into a consideration of the proper method for determining hygroscopic moisture, nor into a study of the physical conditions which limit or enhance the powers of soils to absorb hygroscopic moisture from the atmosphere, because it is almost impossible in laboratory studies to simulate or even nearly to approximate a simulation of field conditions and therefore in our opinion the method which will give an accurate

[1] Society for the Promotion of Agricultural Science, 1882, p. 118.

[2] See Hilgard, in publication just cited, for fuller discussion.

measure of soils with respect to their hygroscopic powers is the only one that is tenable. That at least will indicate the maximum hygroscopic powers of soils and give us relative hygroscopic coefficients of soils which will be of very considerable practical, as well as theoretical value. For a further interesting practical consideration of the value of hygroscopic moisture to plants and the importance of the proper method for its determination, we beg to refer the reader to Hilgard's "Soils," p. 214, in which is to be found a table which correlates the condition of plants in various soils with various amounts of water. The data there presented speak for themselves.

Conclusions

(1) It is necessary to use thin layers of soils in determining their hygroscopic coefficients. A layer as nearly as possible 1 mm in depth has been found the best. Hilgard's method above described for the determinations is recommended to be used as a standard in all soil work on hygroscopicity.

(2) A rise in temperature is accompanied by a greater absorption of hygroscopic moisture. A fall in temperature by a decreased absorption. These do not take place according to any definite law.

(3) For the arid regions in particular, the hygroscopic moisture in soils has a certain definite practical importance.

(4) Similar results on the effect of temperature on the absorption of hygroscopic moisture by soils are obtained in the incubator as in the room. The total absorptions in the incubator, however, as well as the variations with temperature are much smaller than in the room.

We take occasion here to express our sincere thanks to Dr. E. W. Hilgard for kindly criticism and helpful suggestions in these investigations.

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THE ELECTROLYTIC CORROSION OF SOME METALS

BY G. R. WHITE

Electrochemists have paid more attention to the precipitation of metals at the cathode than to the corrosion of metals at the anode. This is not to be wondered at because a good adherent deposit at the cathode is absolutely essential for accurate determinations in electro-analysis and for the success of all processes for the electrolytic refining of metals. For these refining processes, a good even corrosion of the anode with the loss due to mechanical disintegration reduced to a minimum is all that is necessary. In the electro-analysis of metals, these problems do not enter at all because insoluble anodes are always used. As a result of this greater interest in deposition, no systematic study of electrolytic corrosion or dissolution of the anode has been made. However, the anodic behavior of iron,[1] chromium,[2] nickel[3] and cobalt[4] has been studied with completeness to throw some light, if possible, on the question of their passivity. The anodic behavior of copper[5] in neutral and acid copper sulphate solutions has also been studied with care.

In this paper, a study has been made of the electrolytic corrosion of zinc, copper, tin, cadmium, iron, and nickel in solutions of sodium acetate, tartrate, chloride, sulphate, and nitrate. As a rule, the concentration of the electrolyte was

[1] Heathcote: Jour. Soc. Chem. Ind., 26, 899 (1907). Byers: Jour. Am. Chem. Soc., 30, 1718 (1908). Schoch and Randolph: Jour. Phys. Chem., 14, 719 (1910).

[2] W. Hittorf: Zeit. Elektrochemie, 4, 482 (1898); 6, 6 (1899); 7, 168 (1900).

[3] LeBlanc and Levi: Boltzmann's Festschrift, 185 (1904); Levi: Gazz. chim. ital., 35, 391 (1905). Schoch: Trans. Am. Electrochem. Soc., 14, 99 (1908). Byers: Loc. cit. Schoch: Am. Chem. Jour., 41, 232 (1909). Schoch and Randolph: Jour. Phys. Chem., 14, 719 (1910).

[4] Byers: Loc. cit.

[5] Wohlwill: Zeit. Elektrochemie, 9, 311 (1903); Foerster: Ibid., 5, 511 (1899).

75 grams of C. P. salt per liter. If the salt was hydrated, no correction was made for the water of crystallization. Some experiments were also made with a concentration of 25 grams per liter but no special points of interest were found by this variation of concentration. The electrolysis was carried on at room temperature, unless otherwise specified, in a special stirring device in which it was possible to run five determinations in series. By this device the anode was rotated, thus ensuring a thorough mixing of the anode and cathode products. In every case, before the run was made, the anode was filed, scoured with carborundum paper, rinsed with distilled water and absolute alcohol, dried in air and then in a desiccator over calcium chloride for an hour before weighing. The filing and scouring ensured a clean surface for each run. After weighing, the anode was placed in the electrolyte with a platinum or nickel wire for cathode and a current was passed through for a certain time. In each experiment, the current was determined by a copper coulometer which was run in series with the electrolytic cells. An ammeter was also placed in the circuit for control of the current during the run. The electrolysis at room temperature was carried on in 200 cc of electrolyte placed in thick-walled glasses to prevent breakage. The electrolysis was conducted without porous cups, so the electrolyte and the resulting precipitate were subjected to the action of the gases liberated at the electrodes. The anodes and the cathode of the coulometer were always kept in desiccators both before and after electrolysis to protect them from moisture and oxidation.

At the conclusion of the run, the cathode of the coulometer was rinsed with distilled water and absolute alcohol, allowed to dry in air and then in a desiccator for an hour and the gain in weight determined. The cathode was never dried with bibulous paper nor heated to remove the water and alcohol. By following this procedure, the weight of the cathode did not change, even on standing in the desiccator for extended periods of time. The anodes were cleaned by removing the adhering precipitate with a glass rod covered with rubber tubing, by

rubbing with a piece of wood or by a stiff bristle brush. Chemicals were never used in removing the precipitate from the anode. After the anode had been cleaned as thoroughly as possible by the methods specified, it was rinsed with water and absolute alcohol, dried in air and then in a desiccator for an hour and the loss in weight determined. By expenditure of time and energy, the adhering hydroxide could be removed almost completely from the anode. This method does not give the actual loss because some of the precipitate is certain to adhere. There will, however, always be some loss at the anode due to mechanical disintegration and this will appear in the results as corrosion. These two errors tend to compensate each other. If the corrosion was higher than expected, the precipitate was examined to see if any pieces of metal had dropped off. As a further check, the precipitate was dissolved in dilute acetic acid and then hydrochloric acid was added to see if any gas was given off by the particles which did not dissolve in acetic acid. As a rule, there was little or no gas evolution to indicate the presence of metallic particles. There was never enough of the metal present in the precipitate to account for the excess corrosion. Wohlwill[1] has shown that with copper electrodes in sulphuric acid the loss by mechanical disintegration may reach 23 percent. In all of the cases studied, the loss due to this cause never reached this figure and is, in fact, very small.

The results given in the subsequent tables are expressed as percentage current efficiency. The theoretical anode loss is calculated from the following proportion: equivalent weight of copper (31.8): equivalent weight of metal X = gain in weight of copper cathode: loss in weight of the anode of metal X. Theoretically, the gain in weight at the cathode should just equal the loss in weight at the anode. In the proportion above, it is assumed that this is true. As a matter of fact, the anode loss in the copper coulometer is always greater than the cathode gain because some of the copper

[1] Wohlwill: Zeit. Elektrochemie, 9, 311 (1903).

dissolves as the cuprous salt as Foerster and Seidel[1] and Richards,[2] Collins and Heimrod have shown. On the other hand, the anode loss may be very much less than the theoretical cathode gain as shown by all the metals which become passive. The ratio of the theoretical, *i. e.*, 100 percent loss at the anode and the actual loss will give the percentage current efficiency of the corrosion.

The coulometer solution was made up of 150 grams of crystallized copper sulphate, 50 grams of concentrated sulphuric acid and 50 grams of alcohol dissolved in a liter of water. The addition of alcohol is said by Oettel[3] to be especially advantageous if currents of less than one ampere are to be used. The size of the cathode depended on the current strength and was always well within the limits given by Foerster,[4] *i. e.*, not more than 0.02–0.03 and not less than 0.005 ampere per sq. cm of surface. When the current was small, only one anode was used; but, with larger currents, the cathode was suspended between two anodes. Some comparison runs were made with one and with two anodes in the coulometer. It was found that the increase in weight of the cathode was the same in each case for currents of 0.3–0.5 ampere. As an extra precaution, the anode was cleaned with nitric acid and rinsed with distilled water before beginning a run. As a result of the precautions taken, very bright and adherent deposits were obtained. If the deposit was not satisfactory, the run was rejected. The results with the copper coulometer are sufficiently accurate for this work because according to Lehfeldt[5] an accuracy of 0.2–0.3 percent can be obtained without taking any special precautions. If the coulometer is to be used for determining the current, the time must be recorded. One ampere passing through

[1] Foerster and Seidel: Zeit. anorg. Chem., 14, 106 (1897).
[2] Richards, Collins and Heimrod: Zeit. phys. Chem., 32, 321 (1900).
[3] Oettel: Chem.-Ztg., 17, 543, 577 (1893).
[4] Foerster: "Electrochemie wässriger Lösungen," p. 41.
[5] Lehfeldt: "Electrochemistry," Vol. I, p. 10.

the solution for 1 hour will deposit 1.186[1] grams of copper.

When an attackable metal is made anode in a solution of a sodium salt, the anions liberated there will form the corresponding salt of the metal. If the salt thus formed is soluble, it will diffuse away and will react eventually with the sodium hydroxide which is formed at the cathode. Stirring during electrolysis ensures a complete mixing of the anode and cathode products and in most cases a precipitate of the hydroxide will be formed. Lorenz[2] has, in fact, used this method to prepare the hydroxides of several metals. The anode has a very characteristic appearance which depends on the metal and the electrolyte.

Zinc

The corrosion of zinc was first studied under the conditions previously described. The zinc anodes were made from zinc rods which contained a trace of iron but were free from arsenic and carbon. The electrodes were numbered and were changed around from one electrolyte to another in successive runs to obviate any possibility of the surface of the metal influencing the results. Thus, if comparable results were obtained by using different anodes in the same electrolyte, it is presumable that the corrosion noted is due to the electrolyte and not to the electrode. Suppose an electrode is composed of metal which corrodes very easily and this is made anode in one electrolyte constantly, the results would show a greater efficiency of corrosion than is actually due to the electrolyte. By changing the electrodes, results closer to the average corrosion in a given electrolyte will be obtained.

A very important factor in all the work is the condition of the anode surface. During one run a surface may be exposed to the electrolytic action which dissolves readily while during the next run the surface may be very resistant to attack. Metals are seldom homogeneous and any segregation of the impurities, any difference due to the size of the

[1] Richards, Collins, and Heimrod, Loc. cit., give 0.00032915–0.00032925 gram per ampere second or 1.18494–1.18530 grams per ampere hour.

[2] Lorenz: Zeit. anorg. Chem., 12, 436 (1896).

crystals, or any difference brought about by stress during cooling in the mould may affect the rate at which corrosion takes place. According to Andrews, the effect of stress on iron is to cause the metal to dissolve less readily. The same results were obtained by Walker and Dill[1] with Swedish iron in a solution containing ferrous sulphate and potassium chloride when the iron was subjected to stresses up to 31,000 pounds per square inch. This effect is at best very small and doubtless has little or no influence on the corrosion of metals under the conditions holding in this work.

The results of the electrolysis with the larger current were as follows: In the chloride, sulphate and acetate solutions, a heavy white precipitate of zinc hydroxide was formed. The anode surface, after the adhering hydroxide and a thin, black, non-adherent film were removed, was flaky and clean but very slightly darkened. In the tartrate solution, no precipitate was formed because the hydroxide is soluble in sodium tartrate. The anode was coated with a black adherent layer; and a hard white ring, which can be removed, was formed at the surface of the electrolyte. In the nitrate solution, a white precipitate was formed. The anode was pitted with very small depressions which were filled with the white precipitate and presented a "speckled" appearance. It was difficult to remove all this hydroxide, and this fact may account for the lower values obtained for the corrosion in this solution. In all five electrolytes, spongy metallic zinc was formed at the cathode. The filtered supernatant liquid in all cases was alkaline to litmus paper. This may be due to selective adsorption of the acid radical by the colloidal precipitate, thereby leaving the supernatant liquid alkaline. Sodium acetate and tartrate are, of course, alkaline to litmus. Hydrogen was evolved at the cathode in all the solutions. With sodium nitrate, the quantity of hydrogen evolved was small and it was found that nitrites were formed by this cathodic reduction. This reduction would be aided by the presence of the spongy zinc at the cathode. The presence

[1] Walker and Dill: Trans. Am. Electrochem. Soc., 11, 153 (1907).

of this zinc at the cathode may be due either to reduction of the hydroxide by the nascent hydrogen or to the formation of some zincate from which the zinc would be precipitated by the current.

The following table gives the numerical results for the zinc with the larger current. The actual loss in weight and the percentage efficiency of corrosion as calculated by the above proportion are given. The subscripts are the electrode numbers and the order in which the test piece was anode in the different electrolytes may be followed.

TABLE I—ZINC

At. wt. 65.4; equivalent weight, 32.7
Average anode surface, 12.5 cm^2

Run	Cathode coulometer	100 percent Zn	Time	C. D. amp/dm^2
1	0.5252	0.5401	1 hr.	3.5
2	0.4278	0.4399	1 hr.	2.9
3	0.3998	0.4111	1 hr.	2.7
4	0.6805	0.6998	1 hr.	4.6
5	0.3526	0.3626	1 hr.	2.4

Run		NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_3C_4H_4O_6$
1	g.	0.5486_1	0.5494_2	0.5228_3	0.5496_4	0.5468_5
	%	101.6	101.7	96.8	101.7	101.2
2	g.	0.4494_1	0.4492_2	0.4304_3	0.4462_4	0.4056_5
	%	102.2	102.1	97.8	101.4	92.2
3	g.	0.4164_4	0.4214_5	0.3608_1	0.6694_3	0.3932_2
	%	101.3	102.5	87.8	162.8	95.6
4	g.	0.7092_4	0.7116_5	0.7684_1	0.7242_3	0.5846_2
	%	101.3	101.7	109.8	103.5	83.5
5	g.	0.3684_1	0.3710_4	0.2900_3	0.3674_6	0.3516_5
	%	101.6	102.4	80.0	101.3	97.0

The electrolysis was run on the 110 volt direct current which fluctuates markedly because of a variable load, due to turning on and shutting off projection lanterns. This accounts in part for the difference in the amounts of copper deposited in the coulometer. Any hydroxide which adhered

to the anode would affect the resistance of the circuit and therefore the current.

It will be seen that, in many cases, the percentage corrosion exceeded the theoretical value, 100. This may be accounted for by mechanical disintegration and by "local action" between impurities in the zinc and pure zinc, and by zinc in different physical states. Examination of the precipitates for metallic particles showed that the loss due to this cause was very small and will not account for the excess corrosion. Doubtless, part of this excess corrosion was due to "local action" and there is a faint possibility that some of the metal may dissolve with a lower valence than two which would, of course, increase its electrochemical equivalent.

In run 3, the anode in the acetate solution showed a corrosion of 162.8 percent. The average corrosion was about 102 percent. A very much heavier precipitate of the hydroxide was noted and the amount of mechanical disintegration was small. This large excess may then be due to an easily soluble stratum of metal or to error.

Table II gives the numerical results for zinc with the smaller current.

TABLE II—ZINC
Low current densities

Run	Cathode coulometer	100 percent Zn	Time	C. D. amp/dm²
1	0.2352	0.2419	5 h. 25 m.	0.3
2	0.1796	0.1847	4 h. 35 m.	0.26
3	0.2018	0.2075	5 h. 30 m.	0.25
4	0.1808	0.1859	5 h.	0.24

Run		NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g.	0.2464_5	0.2456_3	0.1866_1	0.2382_1	0.2128_2
	%	101.9	101.5	75.4	98.5	88.0
2	g.	0.1942_5	0.1916_3	0.1550_1	0.2014_1	0.1852_2
	%	105.2	103.8	66.7	109.1	100.3
3	g.	0.2108_5	0.2076_3	0.1600_4	0.2008_1	0.1956_2
	%	101.6	100.4	77.1	96.8	94.3
4	g.	0.1876_5	0.1842_3	0.1448_6	0.1742_1	0.1840_2
	%	100.9	99.1	76.1	93.7	99.0

The general appearance of the anodes was about the same as with the higher current densities and precipitation took place in the same solutions. In the chloride and sulphate solutions, the percentage corrosion was about the same with both current densities. In acetate solution, it was not quite so great with the lower current density as with the higher. In the tartrate solution, the corrosion was about the same in both cases. This is peculiar because sodium tartrate has a marked solvent action on zinc and it would be expected that chemical corrosion would aid the electrochemical and thus give a greater loss on longer exposure to the solvent action of the tartrate. In sodium nitrate, the corrosion by the small current was very much less than by the large.

Copper

The corrosion of copper rods was studied in the same electrolytes, and the effect of concentration and temperature as well as current density was also considered. The copper was 99.93 percent pure. The results with the larger current were as follows: In the chloride solution, the anode was covered with a non-adherent brick-red coating of cuprous oxide which could be easily removed, leaving a bright clean surface. The precipitate was orange-yellow cuprous hydroxide with some red cuprous oxide scattered through. In the sulphate solution, the anode was covered with a non-adherent coating of cuprous oxide, easily removable, leaving a surface which was less bright and clean than the chloride. The precipitate was a dirty green color with blue scattered through. In the nitrate solution, the anode was much like the anode in the sulphate solution but was darker. The precipitate was about the same as in the sulphate solution. In the acetate solution, the anode was clean and bright. The precipitate was blue with some black scattered through. In the tartrate solution, the anode was covered with an olive-green coating which could be removed in part, although some adhered, leaving a darkened surface. At the surface of the electrolyte, a hard adherent blue ring was formed which could be removed com-

pletely, leaving the surface slightly roughened. The olive-green coating increased the resistance of the circuit markedly. No precipitate but a deep blue solution was formed, since copper hydroxide is soluble in alkaline tartrate solution. In all cases, the filtered supernatant liquid was alkaline to litmus paper. At the cathode, some metallic copper was deposited. There was also formed at the cathode some cuprous oxide which was intermixed with spongy metallic copper. This metal may come from the reduction of the hydroxide by hydrogen.

The following table gives the numerical results for copper with the larger current.

TABLE III—COPPER

At. wt. 63.6; equivalent weight, 31.8
Average anode surface, 18 cm²

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.449	0.449	1 hr.	2.1
2	0.3996	0.3996	1 hr.	1.8
3	0.5298	0.5298	1 hr.	2.5
4	0.3678	0.3678	1 hr.	1.7

Run		NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g.	0.7542_5	0.4798_1	0.5018_2	0.1570_3	0.2768_4
	%	167.9	106.9	111.8	35.0	61.6
2	g.	0.8022_5	0.4342_1	0.4560_2	0.1342_3	0.2418_4
	%	200.7	108.7	109.0	33.6	60.5
3	g.	1.0722_3	0.5606_1	0.6098_1	0.1672_5	0.3800_2
	%	202.4	105.8	115.1	31.6	71.7
4	g.	0.7448_2	0.390_1	0.4234_5	0.108_3	0.2186_4
	%	202.5	106.0	115.1	29.4	59.4

With the smaller current, the appearance of the anodes was somewhat different from that with the larger current. In the chloride solution, the anode was not quite so clean and bright after the red oxide had been removed. In the sulphate solution, the anode was covered with easily removable cuprous

oxide, but the surface was appreciably darkened. In the nitrate solution, the anode was covered with an easily removable green coating, leaving the surface coated with an adherent chocolate-colored oxide. In the acetate solution, the anode was again clean and bright. In the tartrate solution, the anode was striped and had a definite gold color while at the surface of the electrolyte the blue ring was again formed. The cathodes appeared about the same with these current densities as with the higher. The precipitates had the same general appearance in both cases except in the acetate solution where the precipitate was more greenish blue than with the lower current density. The filtered supernatant liquid was again alkaline. In the nitrate solution, nitrite was again found. Nitrites were always tested for by the potassium iodide and acetic acid method.

Table IV gives the numerical results for copper with the smaller current.

TABLE IV—COPPER

Low current densities

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.2703	0.2703	5 h. 30 m.	0.23
2	0.2944	0.2944	6 hr.	0.18
3	0.2429	0.2429	5 hr.	0.23
4	0.2655	0.2655	5 h. 30 m.	0.23

Run		NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g.	0.5496_2	0.3054_1	0.2246_5	0.0488_3	0.277_1
	%	203.3	0.113	83.1	18.1	102.5
2	g.	0.5962_1	0.3316_2	0.2588_5	0.0702_3	0.2984_1
	%	202.5	112.6	88.0	23.8	101.4
3	g.	0.4992_8	0.2752_7	0.207_8	0.0528_9	0.2514_{10}
	%	205.5	113.3	85.2	21.7	103.5
4	g.	0.5398_6	0.3012_7	0.225_8	0.0450_{10}	0.271_9
	%	203.3	113.4	84.7	16.9	102.1

Comparison of the results in Tables III and IV show that with both current densities the corrosion in the chloride

solution was about the same. The efficiency of 200 percent is accounted for by the fact that in chloride solutions copper dissolves at the anode in the cuprous form while the results are calculated with copper as a bivalent metal. Apparently, the corrosion was slightly more efficient with the small current. This may be accounted for to some extent by the solvent action of the electrolyte on the metallic copper, especially on the longer exposure of the electrolyte to the air. Tilden[1] and Carnelley[2] have shown that sodium chloride containing air in solution has a marked solvent action on copper. In the sulphate solution, the corrosion with the lower current density was also somewhat higher than with the higher current density. In the nitrate solution, the corrosion was markedly less with the lower current than with the higher, and this is doubtless due to the formation, with the low current density, of an adherent oxide film which protects the electrode from corrosion. In the tartrate solution, the corrosion with the low current was very much greater than with the higher current and may be explained by the fact that with the latter the oxide or basic tartrate was formed at the anode faster than the sodium tartrate could dissolve it. This substance, by adhering to the anode, cut down the efficiency of the corrosion. In the acetate solution, the corrosion with the large current was appreciably greater than with the small current and in both cases, a clean bright surface resulted after electrolysis.

Some experiments were carried on with electrolytes containing 25 grams of the salt per liter instead of the 75 grams which was used in the other runs. Both high and low current densities were used. With the higher current density, the anodes in the tartrate solution became coated with the olive-green deposits which increased the resistance so much that the current was cut off almost completely. If the current was shut off, the electrodes, on being allowed to stand in the solution, were depolarized, and if the current were turned on again,

[1] Tilden: Jour. Soc. Chem. Ind., 5, 84 (1886).
[2] Carnelley: Jour. Chem. Soc., 30, 1 (1876).

electrolysis took place only to be followed by polarization and complete stoppage of the current. For this reason, it was impossible to obtain any results for the corrosion of copper in this dilute tartrate solution with the higher current density. However, some measurements were made with the dilute solutions of sodium nitrate and sodium acetate. The results are given in the following table with some results for the sodium tartrate solution (75 grams per liter).

TABLE V—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.5968	0.5968	1 hr.	2.8
2	0.3781	0.3781	1 hr.	1.8
3	0.3349	0.3349	1 hr.	1.6

Run	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$ (75 grams per liter)
1	g. 0.6349_2 % 106.4 g. 0.642_5 % 107.6	0.4734_3 79.3	
2	g. 0.4212_8 % 111.4	0.2179_{10} 57.6	0.2158_6 57.1
3	g. 0.4045_{10} % 120.8	0.2175_7 64.9 0.233_8 69.6	0.2403_9 63.5 0.2022_6 60.4 0.217_9 64.8

The corrosion in sodium nitrate solutions of both concentrations was about the same. The corrosion in the dilute sodium acetate solution was much greater than in the more concentrated solution. The appearance of the anode was about the same in both concentrations of the nitrate. The anode in the dilute acetate solution was pitted and darkened slightly, but still fairly clean.

Runs were also made with copper anodes in the dilute solution with the low current density. The results follow.

TABLE VI—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.1929	0.1929	5 hr.	0.18
2	0.2388	0.2388	6 hr.	0.19

Run	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.157_3 % 81.4 g. 0.1542_1 % 79.9	0.1794_3 93.00 0.1664_2 82.3	0.1966_4 104.3
2	g. 0.1835_1 % 76.8	0.1787_8 74.8 0.1778_7 74.4	0.2585_{10} 108.2 0.1981_8 82.9

With the small current density, the tartrate showed no tendency to polarize and dissolved with high efficiency, giving a good clean anode surface and a deep blue solution. In run 2, with anode 6, the resulting solution was not clear but contained a suspension of cuprous hydroxide. The anode surface was not as clean as those in the other runs. The corrosion efficiency in sodium nitrate was again lower with the low current density and the adherent chocolate-brown oxide was again formed on the anode. The corrosion in sodium acetate showed fluctuation but was somewhat higher with the small current than with the large current. This behavior is just the reverse of the behavior in the more concentrated solution.

Effect of Increased Temperature

It has been shown by Richards, Collins and Heimrod[1] that copper, when heated with copper sulphate in the warm limb of their "circulation apparatus," is dissolved with the formation of cuprous sulphate which decomposes in the cold limb with the liberation of metallic copper and the reforma-

[1] Loc. cit.

tion of cupric sulphate. The reaction is reversible and is represented by the following equation:

$$Cu + CuSO_4 \rightleftarrows Cu_2SO_4.$$

As a result of this fact, it is presumable that the corrosion will be increased by increasing the temperature, since more of the copper will dissolve in the cuprous form. Experiments were run at 95° in the electrolytes containing 75 grams per liter. The results of two runs are appended.

TABLE VII—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.6413	0.6413	1 hr.	3.0
2	0.558	0.558	1 hr.	2.6

Run		NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g.	1.2959$_7$	0.6995$_8$	0.5321$_9$	0.4337$_4$	0.6595$_6$
	%	202.1	109.1	84.0	67.6	102.8
2	g.	1.1267$_4$	0.6423$_6$	0.4004$_8$	0.3741$_7$	0.5594$_0$
	%	201.9	115.1	71.7	67.0	100.2

The corrosion in the chloride solution was not increased by increasing the temperature. In the sulphate solution, very little if any increase was noted. In the tartrate solution, the increase was about 35 percent. The anodes in these solutions were fairly clean. On the other hand, the anode in the acetate solution was covered with a heavy adherent chocolate-brown oxide. The anode in the nitrate solution was covered with a nearly black oxide and, moreover, was deeply pitted and the depressions were filled with red cuprous oxide. As a result, the corrosion in the acetate solution while greater than at ordinary temperatures was not as great as expected. The corrosion in the nitrate solution was very much less than at ordinary temperatures, and part of this decrease is due to the adhering oxide and to the oxide included in the pits. When the adhering oxide was dissolved in a dilute mixture of sodium

chloride and hydrochloric acid and the anode dried and weighed, the corrosion was found to be:

	$NaC_2H_3O_2$	$NaNO_3$
Run 1	119.6	132.0
Run 2	128.4	161.0

However, as the results stand, the influence of temperature is disappointingly small.

When electrolyzing the tartrate solution with copper anodes, it was noticed that oftentimes a greenish yellow suspension was formed instead of a clear blue solution. When the suspension was allowed to settle, it was found that the supernatant liquid was blue, while at the bottom there settled out an orange-yellow precipitate which proved to be cuprous hydroxide. It was thought at first that this came from sodium chloride in the reagents or from the spattering of sodium chloride on the connectors during previous runs. The reagents contained no sodium chloride and with new connectors the same results were obtained. It was also found that large sheet copper anodes seemed to favor the formation of the cuprous hydroxide. The explanation is simple and interesting. Luther[1] has shown that formic acid is formed by oxidation of the tartrate on electrolyzing Fehling's solution with an insoluble anode. The formic acid reduces the Fehling solution and cuprous hydroxide, one of the products of the reduction, is precipitated. It has been shown that in the tartrate solution there is a tendency for the anode to "go passive," *i. e.*, to act like a noble metal. If any copper anode does act like a "noble metal," the oxygen liberated will oxidize the sodium tartrate, formic acid will be formed, and cuprous hydroxide will be precipitated. If a sheet copper anode became "passive," its large surface would give more efficient oxidizing, and would account for the fact that cuprous hydroxide was formed more readily with the sheet than with the smaller rod electrodes. When a current of 0.3 ampere

[1] Luther: Zeit. Elektrochemie, 8, 645 (1902).

was passed through a sodium tartrate solution for 4 hours with a large platinum anode and a small platinum cathode and then some freshly precipitated cupric hydroxide was added, part of the hydroxide was reduced, forming the orange-yellow cuprous hydroxide. If another portion of the tartrate solution was electrolyzed with a small platinum anode and a large platinum cathode and the same current was passed through for the same length of time, no reduction of the added cupric hydroxide took place. This shows that the reduction was due to the formation of some reducing compound by oxidation at the anode. However, a high anode density favored the formation of cuprous hydroxide when Fehling's solution was oxidized electrolytically with platinum electrodes.

Influence of Surface

Attention has been called to the fact that the condition of the electrode surface is one of the most important, if not the most important factor, which influences the corrosion. Some idea of the variation noticed with different electrodes may be gained from the following table. The electrodes were sheet copper and about 50 cm^2 of surface was exposed to the action of the current. The electrolysis was run in sodium tartrate solutions at room temperature.

TABLE VIII—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.4095	0.4095	1 hr.	0.69
2	0.3917	0.3917	1 hr.	0.66
3	0.455	0.455	1 hr.	0.77

Run	$Na_2C_4H_4O_6$				
1	g. 0.3064$_a$	0.2314$_b$	0.3111$_d$	0.2752^e	
	% 74.8	56.5	76.0	67.2	
2	g. 0.3408$_c$	0.3021$_f$	0.3094$_h$	0.3065$_g$	0.2907$_e$
	% 87.00	77.1	77.0	78.2	74.2
3	g. 0.2488$_e$	0.3564$_f$	0.2761	0.3638$_g$	0.3625$_e$
	% 54.7	78.3	60.7	80.0	79.7

The resistance of the circuit was so greatly increased by the formation of the green slimy coating on the anode that the current was cut down about half during the runs.

The experiment was repeated with the rod electrodes in place of the sheet. The results are given in the following table:

TABLE IX—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.2725	0.2725	1 hr.	1.3
2	0.1533	0.1533	1 hr.	0.72
3	0.2698	0.2698	1 hr.	1.2
4	0.3964	0.3964	2 h. 30 m.	0.74

Run	$Na_2C_4H_4O_6$				
1	g. 0.1523_3	0.1498_4	0.1663_2	0.1588_5	0.1550_1
	% 55.9	55.0	61.0	56.9	56.9
2	g. 0.1134_9	0.1002_4	0.1151_7	0.1128_6	0.1191_8
	% 74.0	65.4	75.1	72.0	77.7
3	g. 0.1722_3	0.1639_4	0.1660_2	0.1657_5	0.1528_1
	% 65.0	62.2	63.0	62.8	57.9
4	g. 0.2451_3	0.2359_4	0.2283_2	0.2311_5	0.2346_1
	% 61.8	59.5	57.6	58.3	59.2

One experiment was run for two and a half hours to see if longer exposure to electrolysis affected the passivity of the electrode and increased the quantity of cuprous hydroxide formed. In this experiment, only one of the solutions showed any of the hydroxide. Other experiments, which were run for three and a half hours, showed that at times the hydroxide was formed while at other times it was not, again emphasizing the importance of the electrode surface on the nature of the products formed by the electrolysis. In every case, if copper dissolved and did not go passive, no cuprous hydroxide was formed.

In the next group of experiments, copper was deposited on the copper rod electrodes from a coulometer solution and then corrosion experiments were run with the copper thus deposited. By using a proper current density, it is presumable

that the copper deposit will be uniform throughout and therefore the factor due to inhomogeneity should have been eliminated. If the deposit was not bright and free from streaks, the electrode was not used. Experiments were conducted at room temperature with sodium tartrate as the electrolyte. In the first run, the percentage corrosion is not given. A small current, 0.09 ampere, was used.

TABLE X—COPPER

Run	Time	C. D. amp/dm²
1	1 hr.	0.42

Run	Electrode	$Na_2C_4H_4O_6$			
1	g. 0.0888_9	0.0905_1	0.0875_2	0.0884_6	0.0835_{10}

Cuprous hydroxide was formed in every case and the results are far from being uniform. One experiment was run with the coulometer in series. The results follow:

TABLE XI—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.065	0.065	3 hr.	0.1

Run	$Na_2C_4H_4O_6$				
1	g. 0.0389_3 % 59.8	0.0393_1 60.5	0.0394_2 60.6	0.0364_5 56.00	0.0362_{10} 55.7

It was thought that the lack of uniformity in the results might have been due to the fact that the surface of the anode in the tartrate solution was slightly discolored and also to the fact that at the surface of the electrolyte there was formed a hard ring of bluish green precipitate which might not have been removed completely. Sodium chloride solutions give a very clean anode and therefore some experiments were tried

using it as the electrolyte. The copper was again deposited on the rods from the coulometer solution. In all these cases, more copper was deposited than dissolved off. The results are as follows:

TABLE XII—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm$_2$
1	0.2014	0.2014	1 hr.	0.94
2	0.1437	0.1437	1 hr.	0.67

Run	NaCl				
1	g. 0.4061_1	0.4064_2	0.4066_3	0.4066_5	0.4062_{10}
	% 201.6	201.8	201.9	201.9	201.7
2	g. 0.2893_1	0.2896_2	0.2893_3	0.2907_5	0.2905_{10}
	% 201.3	201.5	201.3	202.3	202.1

The results in run 1 are very satisfactory while those in run 2 show discrepancies.

The results obtained with freshly deposited copper are not much more satisfactory than the results obtained with copper with no other precaution than filing the surface. This is shown in the following table.

TABLE XIII—COPPER
Electrodes filed

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.2628	0.2628	1 hr.	1.22
2	0.2864	0.2864	1 hr.	1.33
3	0.2946	0.2946	1 hr.	1.37

Run	NaCl				
1	g. 0.5322_4	0.5308_6	0.5306_7	0.5210_8	0.5326_9
	% 202.5	202.0	202.9	198.3	202.7
2	g. 0.580_4	0.5720_6		0.5742_8	0.5642_9
	% 202.5	199.7		200.5	197.0
3	g. 0.5934_4	0.5936_6	0.5944_7	0.5878_8	0.5944_9
	% 201.4	201.5	201.8	199.5	201.8

These results seem to show that apparently a uniform surface cannot be obtained by deposition from coulometer solution or else the surface is not as important a factor as expected. The anodes which were prepared by filing were less discolored after the electrolysis than those upon which copper had been deposited.

In the electrolysis of nitrate solutions, nitrite was found in all cases. The presence of the nitrite might aid in the formation of the cuprous salts at the anode. Therefore, experiments were tried to see if the corrosion in sodium nitrite solutions (75 grams per liter) was greater than in nitrate. At the same time, the corrosion in ammonium nitrate solution was also studied. Since copper salts form soluble compounds with ammonium salts, it would be expected that the corrosion would be somewhat higher than with sodium nitrate because the surface of the anode would be kept cleaner. Such was not the case as the results show. One electrode was run in sodium nitrate for comparison.

TABLE XIV—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.6443	0.6443	1 hr.	3.0
2	0.480	0.480	1 hr.	2.2

Run	$NaNO_3$	NH_4NO_3	$NaNO_3$
1	g. 0.7656_1 % 118.8	0.6709_2 104.1	0.7928_6 123.1 0.7980_7 123.9 0.8089_9 125.6
2		g. 0.4955_7 % 103.3	0.5835_1 121.8 0.5782_2 120.5 0.5593_6 116.5 0.5820_9 121.2

In the sodium nitrite solution, the anode was coated with blue hydroxide which adhered strongly. Nearer the electrode surface the coating had a very pronounced green color. A greenish black precipitate was formed, the filtered supernatant liquid was alkaline and the odor of ammonia was detected. With ammonium nitrate, the anode was coated with a bluish green hydroxide and under this a very adherent brown oxide coating was formed. A blue solution containing a small amount of blue precipitate resulted. The results show that the corrosion in the sodium nitrite solution was greater than in sodium nitrate, while in the ammonium nitrate it was less than in sodium nitrate.

In sodium chloride, copper dissolves in the cuprous form. Experiments were tried to see how the copper dissolves in sodium bromide and iodide. One anode was run in sodium chloride for comparison. The results are given below.

TABLE XV

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.4314	0.4314	1 hr.	2
2	0.9307	0.9307	2 hr.	2.2

Run	NaCl	NaBr	NaI
1	g. 0.8115_3 % 183.8	0.5385_7 124.8 0.5479_{10} 127.0	0.1287_1 29.8 0.2283_2 52.9
2	g. 1.8028_4 % 193.7	1.1628_2 124.9 1.1284_7 121.2	0.3215_3 34.5 0.2616_{10} 28.1

In the bromide solution, the anode was coated with a non-adherent hydroxide film and after this had been removed the surface was clean and bright. The precipitate was a mixture

of cuprous and cupric hydroxides. In the iodide solution, the anode was covered with a black adherent layer of iodine and under this some cuprous oxide was found. No precipitate was formed but the solution became yellow from the dissolved iodine. In both cases, the copper dissolved in part at least in the cuprous form. In neither case, was the corrosion as high as in the chloride solution. With the iodide, the small corrosion was due to the protecting action of the iodine on the anode.

Nickel

More work has been done on the behavior of nickel as anode than on any other metal except iron. In nickel plating baths, it is necessary that the anode shall dissolve as efficiently as possible and this, doubtless, accounts for the widespread interest in the anodic behavior of nickel. Saint Edmé[1] has shown that nickel becomes passive on immersion in ordinary nitric acid while iron requires immersion in fuming nitric before it becomes passive. He has also shown that nickel does not lose its passivity on passing chemically pure hydrogen over the red hot passive nickel for 7 or 8 hours and that ammonia is formed by the reaction. On the other hand, under these same conditions, iron loses its passivity. Pfanhauser[2] in his book on electroplating brought out the fact that in the plating bath nickel does not dissolve quantitatively according to Faraday's law and also that the amount of nickel which dissolved depended on whether the nickel anodes were rolled or cast. The question as to the influence which the nature of the anode has on the efficiency of corrosion was studied by Brown[3] who used nickel ammonium sulphate (75 grams per liter) for the electrolyte. The electrolysis was carried on at room temperature using 0.45 amp. hour and a current density of 4.12 amp. per sq. foot in each experiment. The results, taken from Table II in his paper, are as follows:

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[1] Saint Edmé: Comptes rendus, 106, 1079 (1888).

[2] Pfanhauser: Electroplattierungen, 367 (1900).

[3] Brown: Trans. Am. Electrochem. Soc., 4, 81 (1903).

Nickel anode	Current efficiency of corrosion Percent
Cast, surface ground smooth	46.3
Cast, surface roughened in acid	92.1
Rolled, pure	8.5
Electrolytic	12.6

These results show very plainly the influence of the nature of the anode on the efficiency. The general behavior of nickel anodes has been studied very carefully by LeBlanc and Levi,[1] Schoch[2] and Byers.[3]

The corrosion experiments with nickel were run in the same manner as the other metals. The anodes were made from nickel rods which contained only traces of iron, cobalt and carbon. The results with the larger current were as follows: In the chloride solution, the anode was slightly pitted ("speckled") and somewhat darkened. The precipitate was apple-green nickelous hydroxide. In the sulphate solution, the anode was smooth and coated with a thin light brown film of oxide. The precipitate was a dirty green with black specks of nickelic oxide scattered through. In the nitrate solution, the anode was smooth and slightly tarnished; at the surface of the electrolyte, a black non-adherent ring of nickelic oxide was formed. The appearance of the precipitate was about the same as in sulphate solution except that it contained more black specks of the nickelic oxide. In both sulphate and nitrate solutions, some brown gelatinuous precipitate of the nickelic hydroxide was formed in small quantities by oxidation of the nickelous hydroxide. The anodes in sodium acetate and tartrate were unaffected and no precipitate was formed. In this connection, it is interesting to note that in the nickel plating bath unless some compound is added which can dissolve nickel oxide, it will

[1] LeBlanc and Levi: Loc. cit.
[2] Schoch: Loc. cit.
[3] Byers: Loc. cit.

be formed on the anode.[1] No metal was deposited on the nickel wire cathode in any of the experiments and the filtered electrolyte was alkaline in all cases.

The numerical results with the larger current at room temperature are given in the following table.

TABLE XVI—NICKEL

At. wt. 58.7; equivalent weight, 29.35
Average anode surface, 10.3 cm^2

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm^2
1	0.319	0.3867	1 hr.	3.4
2	0.4611	0.4256	1 hr.	3.8
3	0.5549	0.5121	1 hr.	4.5
4	0.5898	0.5444	1 hr.	4.8
5	1.2138	1.1171	2 hr.	5.0
6	0.9444	0.8716	1 h. 30 m.	5.2

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.3914_{6}	0.0078_{4}	0.0122_{3}	0.0066_{1}	0.0069_{2}
	% 101.2	2.0	3.1	1.7	1.8
2	g. 0.4368_{1}	0.0136_{2}	0.020_{3}	0.0024_{5}	0.0122_{4}
	% 102.6	3.2	4.7	0.6	2.9
3	g. 0.5280_{6}	0.0093_{4}	0.0148_{3}	0.0031_{1}	0.0120_{2}
	% 103.1	1.8	2.9	0.6	2.3
4	g. 0.5765_{11}	0.0160_{8}	0.0105_{7}	0.0020_{10}	0.0095_{6}
	% 105.9	2.9	1.9	0.4	1.7
5	g. 1.1404_{12}	0.0157_{8}	0.0286_{10}		0.0189_{7}
	% 102.1	1.4	2.6		1.7
			0.0297_{11}		
			2.7		
6	g. 0.8837_{10}	0.0120_{8}	0.0258_{11}	0.0137_{18}	0.0198_{7}
	% 101.4	1.4	3.0	1.6	2.3

The results showed that nickel is very little affected by any of the electrolytes except the chloride. It was noticed that a new anode, which was cleaned by scouring with carborundum paper and rinsing in distilled water and absolute alcohol, showed a greater corrosion the first time it was made

[1] Tommasi: Electrochimie, 258.

anode in an acetate solution than in any subsequent run. Since the chloride has such a marked effect, precautions were taken to use salts which were chloride free. The excess corrosion in the case of the chloride cannot be explained by the formation of a nickel salt in which the valence of the nickel is one because Denham[1] has shown by an experiment in which metallic nickel was heated with neutral nickel sulphate in the warm limb of the "circulation apparatus" of Richards, Collins and Heimrod that there was no tendency for the nickel to dissolve and to be precipitated in the cold limb. However, in this, as in some other cases, the anode was coated with a non-adherent powder which may be metal in a very fine state of division accounting for a part of the excess corrosion. The fact has already been brought out that the precipitate, as a rule, contains no metallic particles large enough to dissolve in hydrochloric acid with marked evolution of gas.

The fact that sodium chloride dissolves the nickel quantitatively accounts for the fact that platers usually add a handful of table salt to the plating bath. At one time there were on the market "exciting salts"[2] which were purported to increase the conductivity and to insure a bright adherent deposit. Sodium chloride was a constant ingredient in nearly all these "exciters."

If cast nickel, which contained iron and carbon in fairly large amounts but no copper or tin, was made anode in a solution of nickel ammonium sulphate (60 grams per liter) the average corrosion for three runs was 4.3 percent. The electrolysis was carried on for an hour at room temperature with a current density of 1.5 amperes per dm^2. If 0.15 gram of NH_4Cl was added to the above solution, the same anode showed an average corrosion of 94 percent for three runs when the electrolysis was conducted under the same temperature and current conditions as in the previous case. This ex-

[1] Denham: Jour. Chem. Soc., 93, 833 (1908).
[2] LeRoy: Rev. de chim. ind., 7, 70 (1886).

periment shows how the efficiency is increased by the addition of a chloride.

If sheet nickel was made anode in a solution of nickel sulphate (40 grams per liter), the average corrosion for three runs was 3 percent for a run of an hour at room temperature with a current density of 3 amperes per sq. dcm. Snowdon[1] has shown that it is possible to plate nickel on nickel if the nickel cathode is first reduced by making it cathode in a 3 normal solution of hydrochloric acid using a current density of 8 amp. per dm^2 for four minutes. By this treatment the oxide film is reduced and the nickel can be made to adhere strongly. This suggested a treatment for the nickel anodes and experiments were run in which nickel was made cathode in 4 normal sulphuric acid and reduced for four minutes with a current of 8 amp. per dm^2. Then, after quickly rinsing in distilled water, it was transferred to a solution of nickel sulphate in which it was run as anode for 15 minutes. It was then rinsed with distilled water and made cathode again for 5 minutes in the sulphuric acid. This treatment was repeated until the nickel had been run as anode for an hour. By this treatment the corrosion was increased from 3 to 12 percent. The experiment was conducted at room temperature and the current was determined by taking readings every minute during the time the nickel was acting as anode. The increased corrosion cannot be explained by loss of nickel by solution in the sulphuric acid because experiments showed that the amount of nickel thus dissolved when it was cathode in the acid was only about 0.002 gram an hour. Apparently, during electrolysis in the sulphate solution, the anode underwent some change which caused it to corrode poorly, *i. e.*, "to go passive" and this tendency was overcome, in part, by subjecting the anode to the action of hydrogen from time to time and was overcome almost entirely by the addition of a chloride to the sulphate solution.

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[1] Snowdon: Jour. Phys. Chem., 9, 399 (1905).

Since nickel dissolves quantitatively in chloride solution and only slightly in the other electrolytes, the effect of adding known amounts of sodium chloride solution to the other solutions was tried. When 5 cc of the chloride solution was added to 195 cc of the sulphate solution, the corrosion was increased very markedly. The smallest corrosion noted with this mixed electrolyte of chloride and sulphate solutions was 9 percent; the largest was 100 percent. The average of twenty experiments was 65 percent—a very marked increase over the corrosion in the pure sulphate solution. With pure sulphate solution, the precipitate was green with some black specks of nickelic oxide scattered through and discolored by a gelatinous brown precipitate which is doubtless the nickelic hydroxide. With the "mixed electrolytes," the precipitate contained much more of the black oxide and the brown hydroxide and if the quantity of precipitate was small (*i. e.*, if the amount of corrosion was small), it was in most cases composed entirely of a mixture of the black oxide and brown hydroxide. These nickelic compounds were formed by the oxidizing action of the hypochlorite which was formed when the anode became passive and the chlorine, set free there, reacted with the alkali formed at the cathode. The addition of 5 cc of chloride solution to 195 cc of the acetate solution increases the corrosion from a fraction of a percent to the theoretical value with the precipitation of apple-green nickelous hydroxide. The same quantity of chloride solution added to the tartrate solution increased the corrosion from about 2 to 96 percent. The precipitate in this case also was apple-green. With sodium nitrate, it required the addition of a larger amount of the chloride to overcome the passivity of the nickel. With 5 cc of the chloride, the corrosion was only about 8 percent. It requires the addition of about 15 cc of the chloride to increase the corrosion up to theoretical. In all these cases, the amount of chloride required to make the anode corrode quantitatively varied with the electrode. The results given are the average of a number of experiments. The electrolysis was carried on at room temperature with a

current density of from 3–5 amperes per dm^2. In this group of experiments with the "mixed electrolytes," the tendency of the nickel to become passive was opposed and in some cases overcome by the addition of the chloride. LeBlanc and Levi have shown that the passivity of nickel is also overcome by heating the electrolyte during electrolysis.

With the smaller current, the corrosion was greater in every case, excepting the chloride, than with the larger current. The appearance of the anodes and precipitates was about the same as with the larger current—at least there were no striking points of difference. The results with the lower current density are given in the next table.

TABLE XVII—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm^2
1	0.4304	0.3972	8 hr.	0.28
2	0.2529	0.2334	6 hr.	0.34
3	0.2577	0.2378	6 hr.	0.35
4	0.2946	0.2719	6 h. 40 m.	0.36
5	0.303	0.2797	4 h. 40 m.	0.37

Run	NaCl	Na_2SO_4	NaN_3O	$NaC_2H_3O_2$	$NaC_4H_4O_6$
1	g. 0.4106_5	0.0524_4	0.0324_3	0.011_1	0.0256_2
	% 103.2	13.2	8.2	2.8	6.4
2	g. 0.238_7	0.0486_9	0.0253_8	0.0026_{11}	0.0194_{10}
	% 102.0	20.8	10.8	1.1	8.3
3	g. 0.2452_1	0.0542_2	0.031_2	0.0046_5	0.015_4
	% 103.1	22.8	13.0	1.9	6.3
4	g. 0.2806_1	0.035_2	0.0236_3	0.003_5	0.0138_4
	% 103.2	12.9	8.7	1.1	5.1
5	g. 0.2856_5	0.0452_4	0.0308_3	0.001_1	0.0186_2
	% 102.1	16.2	11.0	0.4	6.6

For sake of comparison, the results obtained by LeBlanc and Levi[1] and Byers[2] are here included. The former workers

[1] LeBlanc and Levi: Loc. cit.
[2] Byers: Loc. cit.

used a 1.5 percent solution which was electrolyzed at room temperature. Their results are given in the following table:

Electrolyte	C. D. amp/dm²	Electrode loss Percent
NaCl	0.5	100.0
$NaNO_3$	0.5	5.0
Na_2SO_4	0.5	2.0
$NaC_2H_3O_2$	0.5	45.0
$NaC_2H_3O_2$	0.42	63.0
$NaC_2H_3O_2$	0.32	42.0

Byers gives the following results with electrolytic nickel on electrolysis at room temperature.

Electrolyte	C. D. amp/dm²	Electrode loss Percent
Na_2SO_4	0.4	74.8
Na_2SO_4	0.4	100.0
Na_2SO_4	0.5	2.0
$NaC_2H_3O_2$	0.5	3.4

These results are uniformly higher and in some cases strikingly higher than the results given in Table XVI.

Some experiments were also made with a very small current, *i. e.*, 3–4 milliamperes. The results show very little increase in corrosion over that noted with the other small current density. It was thought that with this small current the corrosion would be very nearly theoretical because the tendency to become passive was shown to be less the lower the current density. The electrolytes, of course, contained air in solution and this dissolved air may account for the continuance of a partially passive state. The results are given in the following table:

TABLE XVIII—NICKEL.

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm²
1	0.0245	0.0226	10 hr.	0.02
2	0.0391	0.0361	10 hr.	0.03
3	0.0435	0.0382	10 hr.	0.036
4	0.0505	0.0444	10 hr.	0.04

Run	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.0097_4 % 42.9		0.0005_3 2.2	0.002_2 8.8
2	g. 0.0067_2 % 18.6		0.0005_4 1.4	0.0027_2 7.5
3	g. 0.0120_4 % 29.9	0.0073_7 18.6		0.0027_3 6.7
4	g. 0.0118_2 % 25.3		0.0007_4 1.5	0.0027_3 5.8

The amounts of metal lost by corrosion were so small that the results are at best untrustworthy. The loss in the tartrate solution might be due to chemical corrosion since the same loss was obtained in three runs.

Some experiments were also tried with electrolytes containing 25 grams of salt per liter instead of the usual concentration, 75 grams. The corrosion was not greatly different from that in the more concentrated solution. The experiments were run at room temperature. The results are given in Table XIX.

Some runs were made, using ammonium salts as electrolytes in place of the sodium salts. The average results ran a little higher than with the sodium salts, except with the chloride solution. The general increase of the corrosion noted may be accounted for by the fact that the ammonium salts form soluble compounds with nickel hydroxide and this would tend to keep the anodes free from adhering hydroxide thus increasing the possibility of corrosion by removing any insoluble compound which might protect the anodes. The

TABLE XIX—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm²
1	0.3675	0.3392	1 hr.	3.0
2	0.4418	0.4078	1 hr.	3.6

Run	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.0081₄ % 2.4 g. 0.0106₈ % 3.1	0.0107₁ 3.1	0.0012₃ 0.3	0.0181₇ 5.3
2	g. 0.0098₄ % 2.4 g. 0.0131₁ % 3.2	0.0103₆ 2.5	0.0012₂ 0.3	0.0098₃ 2.4

anodes, as a matter of fact, were always much cleaner than with the sodium salts. No precipitate was formed in any of the solutions and after electrolysis the filtered electrolyte was alkaline. The chloride became a blue color, the sulphate and sometimes the nitrate, a very faint green, the tartrate a yellow-brown color which was due to the oxidizing action of the oxygen liberated at the anode on the tartrate solution. The same color was obtained when the tartrate solution was electrolyzed with a large platinum anode. The electrolysis was run at room temperature with the larger current. The results are given in the following table:

TABLE XX—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm²
1	0.470	0.4337	1 hr.	3.8
2	0.4806	0.443	1 hr.	3.9
3	0.5349	0.4937	1 hr.	4.4
4	0.6184	0.5708	1 h. 20 m.	3.6
5	0.6989	0.6451	1 h. 15 m.	4.8

Run	NH_4Cl	$(NH_4)_2SO_4$	NH_4NO_3	$NH_4C_2H_3O_2$	$(NH_4)_2C_4H_4O_6$
1	g. 0.4338_7	0.0618_9	0.0404_8	0.0083_{12}	0.0139_{10}
	% 100.0	11.3	9.3	1.9	3.2
2	g. 0.4445_9	0.0344_8	0.0154_7	0.0037_{10}	0.0313_{12}
	% 100.3	7.8	3.5	0.8	7.1
3	g. 0.4996_{12}	0.0535_8	0.0228_9	0.0049_7	0.0153_{10}
	% 101.2	10.8	4.6	1.0	3.1
4	g. 0.5786_9	0.1321_{12}	0.0172_7	0.0109_8	0.0750_{12}
	% 101.9	23.1	3.0	1.9	13.1
5	g. 0.6473_8	0.0353_7	0.0407_{12}	0.0081_9	0.0218_{10}
	% 100.3	5.5	6.3	1.2	3.4

In sodium chloride, nickel corroded quantitatively. Some experiments were conducted to see what efficiency sodium bromide and iodide (75 grams per liter) would give. The bromide gave about as high an efficiency as the chloride. The precipitate was the apple-green hydroxide and the anode was clean and not greatly discolored. The filtered supernatant liquid was alkaline to litmus. The iodide gave a very much lower efficiency and a large amount of iodine was set free at the anode. The precipitate was colored a deep brown by the iodine. In order to see what the color of the precipitate was, the iodine was dissolved by alcohol. By frequent washing, all the alcohol could be removed and the precipitate was found to be apple-green. During the washing process, the odor of aldehyde was noticed and it was thought that any nickelic compound which might be present might have oxidized the alcohol. It was found later that black nickelic oxide did give the odor of aldehyde when treated with alcohol and that, by long-continued washing, it could be reduced to the green nickelous hydroxide. The results on electrolyzing with the larger current at room temperature are given in the next table.

TABLE XXI—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm²
1	0.325	0.2999	1 hr.	2.7
2	0.3768	0.3477	1 hr.	3.1
3	0.4382	0.4043	1 hr.	3.5
4	0.442	0.408	1 hr.	3.6
5	0.4543	0.4193	1 hr.	3.7

TABLE XXI—(*Continued*)

Run	NaI	NaBr
1	g. 0.1474$_{15}$ % 49.1 g. 0.1164$_{18}$ % 38.8 g. 0.1615$_{17}$ % 53.8	0.3033 101.16 0.3054 101.85
2	g. 0.148$_{12}$ % 42.6 g. 0.1525$_{11}$ % 43.8 g. 0.1458$_{3}$ % 41.9 g. 0.1543$_{6}$ % 44.4	0.352$_{10}$ 101.2
3	g. 0.4048$_{2}$ % 100.1 g. 0.1673$_{6}$ % 41.4 g. 0.4305$_{4}$ % 106.5 g. 0.4309$_{2}$ % 106.6 g. 0.0575 % 14.2	precipitate green precipitate green precipitate green
4	g. 0.1816$_{0}$ % 44.6 g. 0.4457$_{3}$ % 109.3	0.4094$_{2}$ 100.4 0.4082$_{1}$ 100.0 0.4102$_{4}$ 100.5
5	g. 0.1447$_{11}$ % 34.5 g. 0.1585$_{1}$ % 37.8 g. 0.0808$_{10}$ % 18.8 g. 0.0467$_{8}$ % 11.1 g. 0.1738$_{20}$ % 41.4	

The corrosion with the iodide solution showed great fluctuation—again indicating the importance of the surface as a factor

in determining the amount of corrosion. Whenever the corrosion was the theoretical value, the precipitate was green.

For sake of comparison, the corrosion in potassium iodide and bromide solutions as determined by LeBlanc and Levi are given. The 1.5 percent solution was electrolyzed at room temperature.

Electrolyte	C. D. amp/dm²	Electrode loss Percent
KI	0.5	101
KBr	0.5	102

This current density was lower than that used in the above experiments.

Tin

The corrosion of tin was studied under the same conditions as the other metals. The anodes were made from "tin sticks" which were free from lead and copper but contained a trace of iron. In every case, the analyses of all the anode metals were made by following the methods given in Krauch, "The Testing of Chemical Reagents for Purity." The appearance of the anodes after electrolysis was very characteristic. In the chloride solution, the anode was very badly pitted and a deep irregular ring was always gouged out at the surface of the electrolyte. The anode was coated with a black film, most of which came off on cleaning, leaving the surface fairly clean. Despite the pitting—or gouging would perhaps more nearly describe the phenomenon—the amount of metal found in the precipitate was very small. In the sulphate solution, the anode was covered with a light brown oxide which was difficult to remove and which discolored the surface. On drying, it was possible to remove much of the oxide by scraping with the finger nail. The wide discrepancies in the results with the sulphate solution are due, in some measure at least, to the adherence or non-adherence of this oxide to the anode. In the nitrate solution, a heavy grayish brown hydroxide was formed which could be removed by

rubbing energetically, leaving a clean anode surface. In most of the runs this hydroxide layer was 2 mm thick. It was soluble in hydrochloric acid without evolution of gas. In the acetate solution, the anode had a brown and white mottled appearance due to the mixture of the two hydroxides which formed on the anode. They could be removed almost completely, leaving the anode spotted brown and white. In the tartrate solution, a glistening dark brown or black oxide was formed which caused a very marked increase in the resistance of the circuit. Part of this oxide rubbed off but the greater part adhered strongly. In describing the compound which adhered to the anode, the terms oxide and hydroxide are used indiscriminately because no attempt was made to ascertain definitely whether they were hydroxides or hydrated oxides. In all the solutions, except the tartrate, a precipitate was formed which was a mixture of white and brown, the latter indicating that some of the tin dissolves in the tetravalent form. In the nitrate solution, the precipitate had a decided gray tinge and the oxide which adhered to the anode was a more pronounced gray than the precipitate. In regard to this gray-colored compound, Tommasi[1] called attention to the fact that when tin was fused in air, a gray coating was formed on the metal which was a mixture of stannous and stannic oxides. Furthermore, Fuchs[2] has shown that if stannous chloride is added to ferric chloride until the latter loses its color and becomes slightly green and then calcium carbonate is added to the above mixture with gentle heating, a precipitate is formed which he called tin sesquioxide. He described it as a grayish white, slimy solid having the composition Sn_2O_3. This is now believed to be a mixture of stannous and stannic oxides (SnO and SnO_2).

Some metal was deposited at the cathode in all the solutions except the tartrate. The filtered supernatant liquid was alkaline in all cases but not alkaline enough to dissolve a suffi-

[1] Tommasi: Electrochimie, 313.
[2] Fuchs: Jour. prakt. Chemie, 5, 318 (1835).

cient amount of the metal to account for any large excess corrosion.

The numerical results on electrolyzing at room temperature with the larger current are given in the next table.

TABLE XXII

At. wt. 119; equivalent weight, 59.5
Average anode surface, 15.8 cm^2

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm^2
1	0.3366	0.6298	1 hr.	1.8
2	0.4324	0.8095	1 hr.	2.3
3	0.6994	1.3088	1 hr.	3.7
4	0.5832	1.0912	1 hr.	3.1
5	0.4006	0.7496	1 hr.	2.1
6	0.3527	0.6599	1 hr.	1.9
7	0.4462	0.8349	1 hr.	2.4

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.6396_5	0.2668_1	1.2036_2	0.5796_3	0.060_4
	% 101.6	42.4	191.1	92.0	9.5
2	g. 0.8128_5	0.0470_1	1.5498_2	0.3454_3	0.0576_4
	% 100.5	5.8	191.6	42.7	7.1
3	g.	0.3768_1	2.2614_4	0.947_3	0.1100_2
	%	28.8	172.8	72.4	8.4
			2.38_6		
			181.9		
4	g. 1.1002_6	0.3008_1	2.0748_2	0.9264_3	0.0742_4
	% 100.8	27.6	190.1	84.9	6.8
5	g. 0.7622_8	0.6321_9	1.4027_1	0.6642_{10}	0.0552_{12}
	% 101.7	84.3	187.1	88.6	7.4
6	g. 0.6289_4	0.2290_6	1.2075_8	0.562_{12}	0.0473_9
	% 95.3	34.7	183.6	85.2	7.2
7	g. 0.7147_7	0.6025_3	1.344_5	0.7576_3	0.0327_4
	% 85.6	72.2	161.0	90.7	3.9

The results show wide discrepancies in some cases and no definite explanation can at present be offered for the lack of uniformity.

An experiment was tried in which five tin anodes were run in series at room temperature with sodium sulphate as

electrolyte. The anodes had been used in several runs although they were filed before this run according to the usual procedure. The corrosion showed a variation of about 7 percent and was much less than the highest efficiency of corrosion noted. The results are given below.

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm²
1	0.3596	0.6729	1 hr.	1.9

Run	Na_2SO_4				
1	g. 0.2012_1	0.1880_2	0.1896_4	0.210_6	0.2386_6
	% 29.9	27.9	28.2	31.2	35.5

Some of the tin which was used for anodes was found to be honey-combed with "blow holes" some of which were very large. Therefore, it was thought worth while to cast some tin and to use these newly cast sticks for anodes with the hope that these "blow holes" could be obviated by careful casting. Granulated tin (C. P.) was fused in a graphite crucible and cast into sticks (8 cm long × 0.8 cm diam.) in a graphite mould. These sticks were free from "blow holes" but the results obtained on electrolysis at room temperature failed to show uniform corrosion as the following table shows.

TABLE XXIII—TIN (newly cast)

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm²
1	0.5026	0.9404	1 hr.	2.7
2	0.4557	0.8527	1 hr.	2.4

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.8008_a	0.6645_c	1.5037_b	0.869_e	0.0477_d
	% 85.2	72.3	159.9	92.4	5.1
2	g. 0.7818_f	50.81_c	1.3728_b	0.6561^e	0.0024_d
	% 91.7	59.6	161.0	75.4	0.3

The results in the chloride and nitrate solutions ran quite a little lower than the average in the other runs. In the sulphate solution, the corrosion was much higher than it was when the five anodes were run in series and approached the higher values. In the second run, the anode became passive in the tartrate solution. In the acetate solution, the results were about the same.

The corrosion of tin in sodium chloride and sulphate solutions has been studied by Elbs and Thümmel.[1] They used solutions of two concentrations and three different current densities. After electrolysis, the solution was neutral which showed that the hydroxide and not a basic salt was precipitated. The anode was wrapped in cotton cloth to prevent the loss of pieces which fall from the electrode. Their results showed that only about 10 percent of the tin dissolved in the tetravalent form while 90 percent dissolved in the divalent form. Part of their results are here given. The temperature throughout was 18°.

Electrolyte	Concentration Grams per liter	C. D. amp/dm²	Corrosion efficiency Percent
NaCl	117	1.0	98.8
NaCl	117	10.0	99.8
NaCl	5.85	1.0	90.8
NaCl	5.85	10.0	96.5
Na_2SO_4	142	1.0	93.0
Na_2SO_4	142	10.0	94.2
Na_2SO_4	7.1	1.0	95.5
Na_2SO_4	7.1	10.0	94.4

The most striking point in Table XXII is the high corrosion efficiency in the nitrate solution. As stated before, this excess corrosion was not due to mechanical disintegration because the precipitate and adhering oxide dissolved in hydrochloric acid without evolution of gas. The average corrosion was well above 175 percent when the assumption was made

[1] Elbs and Thümmel: Zeit. Electrochemie, 10, 365 (1904).

that all the tin dissolves in the divalent form. Some of the metal dissolved in the tetravalent form, as Elbs and Thümmel have shown, but this would tend to make the results lower rather than higher because the equivalent weight of tetravalent tin is 29.75 while that of divalent tin is 59.5. There is a possibility that some of the tin dissolved in the monovalent form. In the literature, no reference could be found to the existence of any oxide of tin having the formula Sn_2O. However, lead, another metal in the fourth group of the periodic table which is most closely analogous to tin—also a member of this group—forms a suboxide Pb_2O. According to Berzelius, the gray oxide which is formed on the surface of lead when it is exposed to air consists of Pb_2O. Dulong showed that a black powder remained, after the residue had cooled in the retort, when lead oxalate was heated to 300° out of contact with the air until no more gas was given off. When heated in air, this black powder burned to lead oxide. When heated out of contact with the air, it gave lead oxide and metallic lead. When moist, it absorbed oxygen from the air and formed a hydrated lead oxide, $PbO.xH_2O$. On treating the suboxide with dilute acids or with a saturated solution of lead nitrate, it was transformed into lead oxide. It is not a mixture of lead oxide and metallic lead because, when rubbed with mercury either dry or under water, no lead was removed. Furthermore, lead oxide was not removed by boiling with lead acetate. Tanatar[1] has shown that it can also be prepared when lead oxalate is heated in a combustion tube to the lowest possible temperature necessary to decompose the oxalate and a stream of dry carbon dioxide is conducted through the apparatus. He described the substance as a grayish black powder which can be decomposed in the cold when treated with a 10 percent solution of sodium hydroxide which dissolves the oxide and leaves the metallic lead. The specific gravity of this suboxide was different from that of a mixture of lead oxide and metallic lead. Tanatar also

[1] Tanatar: Zeit. anorg. Chem., 27, 304 (1901).

measured the heat evolved when a gram molecule of this compound was dissolved in acetic acid and compared the value thus obtained with Thomsen's value for the heat evolved when lead oxide dissolves in acetic acid. The two values were not the same which is another indication that this is a definite compound. Denham[1] has shown that lead, when heated with lead acetate in the warm limb of the circulation apparatus, is deposited in the cold arm, indicating a reaction which takes place as follows: $Pb + PbC_2H_3O_2 = Pb_2C_2H_3O_2$ and which is a further indication of monovalent lead.

When lead was made anode in a solution of sodium nitrate and the solution was electrolyzed at room temperature, a white precipitate was formed and at the anode a dark gray oxide which could be easily removed leaving the surface clean. The filtered supernatant liquid was alkaline and a spongy deposit of lead was formed at the cathode. The solution also contained large quantities of nitrite. The results are given below.

TABLE XXIV—LEAD

At. wt. 207.1; equivalent weight, 103.55
Average anode surface, 12.5 cm^2

Run	Cathode coulometer	100 percent Pb	Time	C. D. amp/dm^2	$NaNO_2$
1	0.5357	1.7104	1 hr.	3.6	g. 1.8003 % 102.8
2	0.5407	1.7607	1 hr.	3.6	g. 1.8377 % 104.4

The results are very much lower than required to indicate that some of the lead had dissolved in the monovalent form.

The results for the corrosion of tin with the lower current density are as follows. The electrolysis was carried on at room temperature.

[1] Denham: Loc. cit.

TABLE XXV—TIN

Runs	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm²
1	0.1086	0.2032	5 hrs.	0.12
2	0.1062	0.1978	5 hrs.	0.12
3	0.107	0.2003	5 hrs.	0.12

Run		NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$NaC_4H_4O_6$
1	g.	0.1874_5	0.1378_3	0.2686_4	0.0790_1	0.0026_2
	%	92.2	67.8	132.2	38.9	1.3
2	g.	0.145_5	0.0398_3	0.2834_4	0.0724_1	0.001_2
	%	73.3	20.1	143.3	36.6	0.5
3	g.	0.187_3	0.0952_5	0.280_2	0.0628_1	0.0064_4
	%	93.4	47.6	139.8	31.4	3.3

In the chloride solution, the corrosion was about the same as with the higher current density. In the sulphate solution, it was somewhat less than in the other case. In the nitrate, acetate and tartrate solutions, it was quite appreciably less. The appearance of the anodes was about the same in both cases and the filtered supernatant liquid was alkaline. Metal was deposited in all solutions in which it was formed with the larger current.

Curry[1] has shown that the corrosion of bronzes increased very rapidly as the tin content increased. In solutions of sodium sulphate, acetate and alkaline tartrate, the tin-rich bronzes corroded very readily but with increasing amounts of the E phase the corrosion showed a marked decrease. With increasing amounts of pure tin in the bronze, the corrosion was found to increase. In sodium nitrate solution, the corrosion was very much higher than the theoretical, especially as the tin content increased. With pure tin, the corrosion was about 2.5 times the corrosion in the coulometer when the assumption was made that all the tin dissolved in the tetravalent form. The fact that tin corroded readily in sulphate,

[1] Curry: Jour. Phys. Chem., 10, 482 (1906).

chloride and nitrate solutions was also mentioned in this paper. In this work, the electrolysis was carried on at room temperature for 8 hours with a current of 0.025 ampere. The current density was 0.18 amp/dm².

In the sodium nitrate solution, nitrite was formed by reduction as usual. It was thought that the nitrite might increase the corrosion of the tin. Therefore, some experiments were tried with a solution of sodium nitrite (75 grams per liter). Some experiments were also tried with a solution of ammonium nitrate of the same concentration to see how another nitrate affected the tin. The results with the larger current on electrolyzing at room temperature are given in the following table. In the first run, one test was made with sodium nitrate for comparison.

TABLE XXVI—TIN

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm²
1	0.5375	1.0067	1 hr.	2.8
2	0.4727	0.8845	1 hr.	2.5
3	0.4483	0.8388	1 hr.	2.4

Run	$NaNO_3$	$NaNO_2$	NH_4NO_3
1	g. 1.6791_4	0.1137_5	1.6449_2
	% 167.0	11.3	163.6
			1.8875_6
			187.7
2		0.0105_5	1.4910_4
		1.2	168.6
		0.1479_7	1.4519_2
		16.7	164.2
			1.6515_6
			186.7
3		0.085_6	1.5446_5
		10.1	184.1
		0.0987_6	1.3666_7
		11.8	162.9
			1.3248_7
			157.9

In the nitrite solution, only a small amount of the gray-colored precipitate was formed. The anode was covered with a dark adherent oxide and the solution was alkaline to litmus. The corrosion was small and the action of the nitrite formed will not explain the excess corrosion in the nitrate solution. In the ammonium nitrate solution, a heavy white precipitate was formed. The anode was covered by a grayish brown oxide which could be readily removed, leaving a fairly clean surface. In this case also, the filtered supernatant liquid was alkaline to litmus and the odor of ammonia was plainly noted.

Iron

From the time of Keir[1] who discovered that iron when immersed in nitric acid (sp. gr. 1.45) did not dissolve, up to the present time, the passivity of iron has interested chemists. Various explanations have been offered for this phenomenon, ranging from the "oxide film" theory of Faraday and Schönbein[2] to the "velocity of reaction between metal and anodic oxygen" theory of Fredenhagen.[3] Recently Krassa[4] has come forward with experiments from which he concludes that the passivity is due to a "skin of oxide." This conclusion completes a cycle of explanation and theory has again arrived at the first explanation given for passivity, namely, the "oxide film" theory. A very complete bibliography of this subject is given by Heathcote[5] and DeBenneville[6] gives a critical survey of the field up to the time his paper was published.

Assuming that an oxide film was formed, attempts have been made to determine its thickness by a study of its power to reflect polarized light. Micheli[7] showed that this method indicated that the optical properties of the surface

[1] Keir: Phil. Trans., 80, 359 (1790).
[2] Faraday: Expt. researches, 2, 231.
[3] Fredenhagen: Zeit. phys. Chem., 63, 1 (1908).
[4] Zeit. Elektrochemie, 15, 490 (1909).
[5] Heathcote: Loc. cit.
[6] DeBenneville: Jour. Iron and Steel Inst., 52, 40 (1897).
[7] Micheli: Arch. des Sciences, [4] 10, 122 (1900).

of active and passive iron were different. Müller and Königsberger[1] concluded from their experiments that, if the passivity were due to an oxide film, the film must be less than one-tenth of a wave-length thick. Later they showed that the reflecting power of iron mirrors was unchanged when the iron was anode in sodium hydroxide and the current passed until oxygen was evolved (*i. e.*, metal passive) or when as cathode in the same solution, hydrogen was evolved, *i. e.* (metal active).

For sake of comparison, the results of Mott[2] on the thickness of the film which is formed on aluminum anodes in saturated solution of disodium phosphate are here given. By determining the increase in weight and knowing the surface over which the film spread, it is possible to determine the thickness of the film. The following results are taken from his paper.

Voltage	Thickness of film	
	If $Al(OH)_3$ cm	If $AlPO_4$ cm
10	0.000013	0.000025
50	0.000032	0.000063
120	0.000064	0.000126

Other methods of measurement gave comparable results indicating that the film is very thin.

One very interesting fact is that the passivity of iron in concentrated nitric acid is overcome by subjecting the iron to the action of a strong magnetic field.[3] Another interesting fact is Burgess's[4] application of the passive state of iron in removing the film of brass left on bicycle frames after brazing. A solution of sodium nitrate is used as electrolyte and the bicycle frame as anode. The iron becomes passive so does not dissolve while the zinc and copper are

[1] Müller and Königsberger: Phys. Zeit., 5, 413, 797 (1904). Zeit. Elektrochemie, 13, 659 (1907).

[2] Mott: Electrochem. Ind., 2, 268 (1904).

[3] Nichols: Am. Jour. Sci., [3] 31, 272 (1886).

[4] Burgess: Trans. Am. Electrochem. Soc., 4, 31 (1903).

easily soluble. Burgess believes that the presence of nitrite in solution aids the iron in becoming passive.

The corrosion of iron was studied in the same way as the other metals. The anodes were made of iron rods and contained small amounts of carbon, manganese and silicon. After electrolysis, the appearance of the anodes and precipitates was as follows. In both the chloride and sulphate solutions, the anodes were coated with a black film which could be easily removed leaving a bright clean surface. On the anode, at the surface of the electrolyte a small amount of rust appeared which could be removed completely. The precipitate was a dirty, olive-green color indicating that most of the metal had dissolved in the ferrous form. Renault[1] has shown that iron, when in metallic connection with zinc in oxidizing solutions like potassium chlorate or bichromate, acidified with hydrochloric acid, dissolves in the divalent form. In the nitrate, acetate and tartrate solutions, no precipitate was formed and the only change noted at the anode was the formation of a small amount of rust at the surface of the electrolyte. The tartrate solution was colored a very faint yellow. The filtered supernatant electrolyte was alkaline in all cases and no metal was deposited at the cathode. Special precautions were taken to prevent the iron from rusting after removal from the electrolyte at the end of the run. The results at room temperature for the larger current are given in the next table. The efficiency is calculated on the assumption that the iron dissolved in the divalent form.

TABLE XXVII—IRON

At. wt. 55.9; equivalent weight, 27.95
Average anode surface, 13.3 cm^2

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm^2
1	0.4562	0.401	1 hr.	2.9
2	0.497	0.4368	1 hr.	3.2
3	0.5136	0.4514	1 hr.	3.3
4	0.5138	0.4516	1 hr.	3.3

[1] Renault: Ann. Chim. Phys., [4] 11, 150 (1867).

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.4148_1	0.413_3	0.0036_2	0.001_5	0.0008_4
	% 103.4	103.0	0.9	0.2	0.2
2	g. 0.4542_5	0.4544_3	0.0016_4	0.0_1	0.0016_2
	% 104.0	104.0	0.4	0.0	0.4
3	g. 0.469_6	0.4684_3	0.0038_4	0.0_1	0.002_2
	% 103.9	103.8	0.8	0.0	0.4
4	g. 0.4668_1	0.4572_2	0.0014_4	0.0016_5	0.0028_3
	% 103.3	101.3	0.3	0.3	0.6

The results show that the iron dissolved quantitatively in both the chloride and sulphate solutions and remained passive in the nitrate, acetate and tartrate solutions.

The corrosion in the more dilute solution was then studied. The electrolysis was run at room temperature with the larger current. Only those electrolytes in which the iron was passive in the more concentrated solution were studied. The change in concentration did not overcome the passivity as the results which are given in the next table show.

TABLE XXVIII—IRON

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm²
1	0.2726	0.2396	1 hr.	1.7
2	0.3075	0.2703	1 hr.	1.9
3	0.4587	0.4031	1 hr.	2.9

Run	$NaNO_3$	$NaC_2H_3O_2$	$NaC_2H_3O_2$ (75 g. per liter)	$Na_2C_4H_4O_6$
1	g. 0.0017_0	0.0008_3		0.0008_1
	% 0.7	0.3		0.3
	g. 0.0005_7			
	% 0.2			
	g. 0.0015_0			
	% 0.6			
2	g. 0.0023_3	0.0013_1	0.0021_5	0.0014_7
	% 0.9	0.5	0.78	0.5
3	g. 0.0046_0	0.0014_1	0.0025_3	0.0035_1
	% 1.1	0.3	0.62	0.9
	g. 0.0011_7			
	% 0.3			

With the smaller current, the appearance of the anodes and precipitate was about the same as with the larger. The distinctive fact was that with this lower current density the iron dissolved quantitatively in the nitrate solution. Gee[1] has shown that iron dissolves quantitatively in half-normal sodium nitrate until a current density of 3.5 amp/dm² is reached and then with higher current densities it becomes passive. The appearance of the anode and precipitate was about the same as with the chloride and sulphate solutions. The filtered electrolyte was alkaline and no metal was deposited on the cathode. The results at room temperature are given in the next table.

TABLE XXIX—IRON

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm²
1	0.1871	0.1644	5 hr.	0.24
2	0.2055	0.1806	5 hr.	0.26
3	0.2208	0.1941	5 hr.	0.28
4	0.2782	0.2445	5 hr.	0.35

Run		NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g.	0.1761_3	0.1701_1	0.1669_5	0.0005_6	0.0007_3
	%	108.4	103.4	101.5	0.3	0.4
2	g.	0.1886_5	0.1882_4	0.1782_3	0.001_1	0.003_2
	%	104.4	104.2	98.7	0.5	1.7
3	g.	0.1998_1	0.2014_2	0.1934_3	0.0006_5	0.0018_4
	%	102.9	103.8	99.7	0.3	0.9
4	g.	0.2518_1	0.2462_3	0.2436_2	0.001_5	0.0018_4
	%	102.8	100.7	99.6	0.4	0.7

With the current density at which iron dissolved quantitatively in the nitrate solution, it remained passive in the acetate and tartrate solutions. Arth[2] has shown that iron, in a solution of sodium acetate (50 grams per liter) acidified with 50 grams of glacial acetic acid, dissolves quantitatively with a low current density (about 0.009 amp/dm²). He

[1] Gee: Jour. Inst. Elect. Eng., 41, 425 (1908).
[2] Arth: Bull. Soc. chim. Paris, [3] 21, 766 (1899).

also showed that the iron dissolved in the divalent form by adding potassium ferricyanide to the solution directly around the anode. In light of this work of Arth's, it was hoped that a further reduction of the current would cause the iron to dissolve quantitatively in these two solutions. Several attempts with currents of 0.0025–0.003 amperes failed to show any appreciable increase of the corrosion in the unacidified acetate solution. It was noted, however, that in the tartrate solution the corrosion was greater than the theoretical value. The results for electrolysis at room temperature with the more concentrated solution are given in the next table.

TABLE XXX—IRON

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm²
1	0.0245	0.0215	10 hr.	0.020
2	0.0313	0.025	10 hr.	0.025
3	0.0435	0.0382	10 hr.	0.028
4	0.0505	0.0444	10 hr.	0.032
5	0.0575	0.0505	10 hr.	0.036

Run	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$	$NaNO_2$
1	g. 0.0008_3 % 3.7	0.026_4 120.8	
2		0.0018_5 6.5 0.0376_2 136.7 0.0372_1 135.2	0.0367_0 133.4 0.0340_7 123.6
3		0.0_4 0.0 0.0434_2 113.5	
4	g. 0.0005_4 % 1.1	0.06_2 135.2	
5		0.0598_0 118.4 0.0609_7 120.5 0.0602_2 119.1 0.0609_1 120.4	0.0489_5 96.7

The explanation for this excess corrosion in the tartrate solution is found in the fact that iron is appreciably soluble in the tartrate solution and the chemical corrosion therefore aids the electrochemical. When the iron anodes were subjected to the action of the tartrate solution for the same length of time that the run occupied, it was found that the iron was dissolved in amounts which are shown in the next table.

TABLE XXXI—IRON

Chemical corrosion in sodium tartrate solution, *i. e.*,
(Amount of iron dissolved by sodium tartrate solution in 10 hours)

Run	Time	$Na_2C_4H_4O_6$				
	Electrode	1	2	3	4	5
1	10 hr.	0.0101 g.	0.0093 g.			0.0115 g.
2	10 hr.	0.0095 g.	0.0095 g.	0.0115 g.	0.0101 g.	0.0118 g.
		6	7			
1	10 hr.	0.0104 g.	0.0091 g.			
2	10 hr.					

If the quantity of iron dissolved chemically is deducted from the total amount lost by corrosion, it will be found that the corrosion then becomes very nearly theoretical. This is shown by two examples which follow.

	Electrode 2	
Run 2	0.0376 g. — 0.0095 = 0.0281 g.	102.2 %
	Electrode 6	
Run 5	0.0598 g. — 0.0104 = 0.0494 g.	97.75 %

The high corrosion in the nitrate solution was doubtless due to the solubility of the iron in the solution although this was not checked by experiment.

Cadmium

The electrolytic corrosion of cadmium was studied in the same manner as the other metals. Its behavior as anode showed many interesting points. The cadmium used was very

pure and contained only traces of zinc and lead. After electrolysis, the appearance of the anodes and precipitates was as follows. In the chloride and acetate solutions, the anodes were coated with a layer of white hydroxide under which was a film of dark brown oxide. Both could be easily removed leaving the surface clean and bright. In the sulphate solution, the anode was much like the other two anodes but it could not be so well cleaned because of a slight tendency to pitting and a greater tendency for the hydroxide to adhere. In the nitrate solution, the anode was covered by a white sheath of hydroxide which could be removed readily. Under this sheath, a heavy layer of a gray-colored mass was formed, sometimes extending 3 mm from the anode surface. In the tartrate solution, the anode was clean, smooth and bright except for splotchy films of a golden brown oxide. In all solutions except the tartrate, a white precipitate was formed which was especially heavy in the nitrate solution. In the tartrate solution, there was no precipitate because cadmium hydroxide is soluble in sodium tartrate. The filtered supernatant liquid was alkaline and metal was precipitated in heavy, spongy masses in the sulphate, nitrate and tartrate solutions but in only small amounts in the chloride and acetate solutions. The numerical results with the larger current at room temperature are given in the next table.

TABLE XXXII—CADMIUM

At. wt. 112.4; equivalent weight, 56.2
Average anode surface, 18.1 cm^2

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm^2
1	0.3726	0.6585	1 hr.	1.7
2	0.470	0.8306	1 hr.	2.2
3	0.501	0.8854	1 hr.	2.3
4	0.5374	0.9497	1 hr.	2.5
5	0.639	1.1293	1 hr.	3.0

TABLE XXXII—(*Continued*)

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.6648_5	0.6856_4	0.9002_3	0.6654_2	0.6572_1
	% 100.9	104.1	136.7	101.0	99.8
2	g. 0.8324_5	0.8452_4	1.0868_3	0.845_2	0.7636_1
	% 100.2	101.8	130.8	101.7	91.9
3	g. 0.895_1	0.944_5	1.2286_2	0.8968_4	0.8166_3
	% 101.1	106.6	138.8	101.3	92.2
4	g. 0.9556_5	0.8494_3	1.3586_4	0.9026_1	0.9128_2
	% 100.6	89.4	143.1	95.0	96.1
5	g. 1.1404_5	0.9394_3	1.5978_3	1.020_1	1.0576_3
	% 100.9	83.1	112.4	90.3	93.6

The corrosion was very nearly theoretical in all cases except in the nitrate solution in which it was appreciably greater.

One experiment was tried to ascertain how much oxide adhered to the anode by immersing it in acetic acid until all of the oxide was dissolved and then quickly removing and rinsing with water. This gives only an approximation of the actual amount of adhering oxide because some metal will also dissolve. The anodes were run in sodium nitrate solution at room temperature and the loss in grams and the efficiencies both before and after treatment with acetic acid are given in the following table.

TABLE XXXIII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5792	1.0236	1 hr.	2.7

Run	$NaNO_3$			
1	g. 1.4961_1	1.5091_3	1.5068_4	1.489_5
	% 146.2	147.4	147.4	145.4
	Anodes treated with 80 per cent CH_3COOH			
1	g. 1.5178_1	1.5331_3	1.5331_4	1.5156_5
	% 148.3	149.8	149.8	148.1

This table shows that for this experiment, the average loss on treating the anode with acetic acid is 0.0246 gram and the

average increase in corrosion on allowing for this is 2.4 percent. It was more difficult to remove all the adhering oxide from the cadmium anode in the nitrate solution than in any other solution except the sulphate. Therefore, it is likely that the above gain in efficiency is somewhat above the average gain which would be noted if all the anodes were thus treated before final weighing.

The effect of variation of the concentration of the electrolyte on the corrosion in the nitrate and tartrate solutions was also studied. The nitrate was chosen because it gave a corrosion efficiency greater than theoretical; the tartrate because the electrode, at the conclusion of the run, was clean. With the less concentrated tartrate solution, a precipitate was formed. The results with the larger current at room temperature are as follows:

TABLE XXXIV—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.3588	0.6341	1 hr.	1.7
2	0.4423	0.7816	1 hr.	2.06

Run	$NaNO_3$ (75 g. per l.)	$NaNO_3$ (25 g. per l.)	$Na_2C_4H_4O_6$ (75 g. per l.)	$Na_2C_4H_4O_6$ (25 g. per l.)
1	g. 0.8627_4 % 136.1	0.9599_2 151.4 0.8438_8 133.1	0.5832_1 92.0	0.5055_6 79.7
2	g. 1.1151_3 % 142.7	0.969_2 124.0 1.0749 134.4	0.7481_5 95.7	0.5873_1 75.1

The results show that the corrosion was slightly less in the more dilute solution of the nitrate and quite appreciably less in the more dilute solution of the tartrate. The latter may be explained by the fact that a precipitate was formed in this solution and the anode was therefore not kept so clean as

with the more concentrated solution and the possibility of corrosion was cut down by the formation of a precipitate on the anode.

Some experiments were also run with the smaller current at room temperature. The appearance of the anodes in the chloride, sulphate and acetate solutions was about the same as in the previous case. In the nitrate solution, there was a much smaller quantity of the gray mass than with the larger current. In the tartrate solution, the anode was not so smooth and did not have the golden brown splotches observed with the other current strength. The results as regards deposition of metal at the cathode and alkalinity of the filtered supernatant liquid were strictly comparable to the results in the first case. The results are given in the following table:

TABLE XXXV—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.2218	0.392	5 hr.	0.21
2	0.2349	0.4248	5 hr.	0.22
3	0.2415	0.427	5 hr.	0.23
4	0.2616	0.4623	5 hr.	0.25

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.3978_1 % 101.5	0.3964_6 101.1	0.3788_2 96.6	0.4004_4 102.1	0.4086_3 104.3
2	g. 0.420_1 98.9	0.4206_5 99.0	0.4062_2 95.6	0.4236_4 99.7	0.4272_3 101.0
3	g. 0.436_1 % 102.1	0.4404_4 103.1	0.3870_3 90.6	0.4400_5 103.0	0.4576_2 107.9
4	g. 0.4739_1 % 102.5	0.475_3 102.7	0.3782_5 81.8	0.4798_2 103.8	0.482_4 104.3

A comparison of these results with those obtained with the larger current shows that in the chloride solution, the corrosion was about the same in both cases. With the acetate and sulphate solutions, it was a trifle higher and with the tartrate solution appreciably higher with the smaller current. On

the other hand with the nitrate solution, it was markedly lower with the smaller current.

The most striking fact noted in this work on cadmium was the high corrosion efficiency in the nitrate solution. The question arose as to whether this was a property peculiar to sodium nitrate alone or whether it was also shared by other nitrates. To settle this question some experiments were run with cadmium nitrate (75 grams per liter) and ammonium nitrate (75 grams per liter). With the former, no precipitate was formed except that which falls from the anode, large amounts of spongy metallic cadmium are deposited at the cathode, and the solution remained neutral. At the anode, large quantities of the gray mass were formed without the intervention of an hydroxide. The solution also contained a large quantity of nitrite. The results with cadmium nitrate at room temperature with the larger current are given in the next table. In Run 1, two anodes were run in sodium nitrate solutions of the two concentrations for purposes of comparison.

TABLE XXXVI—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.4999	0.8835	1 hr.	2.3
2	0.4455	0.7873	1 hr.	2.1

Run	$NaNO_3$ (75 g. per l.)	$NaNO_3$ (25 g. per l.)	$Cd(NO_3)_2$ (75 g. per l.)
1	g. 1.2709_5	1.2590_1	1.2462_2
	% 143.8	142.5	141.0
			1.2491_3
			141.4
			1.2583_4
			142.4

Run	$Cd(NO_3)_2$				
2	g. 1.1179_1	1.1364_2	1.1470_3	1.1375_4	1.1499_5
	% 142.0	144.3	145.7	144.5	146.1

The corrosion in the cadmium nitrate solution was about the same as in the sodium nitrate, indicating that the large corrosion noted is a property of the nitrates and not of sodium nitrate alone.

The corrosion in ammonium nitrate was next studied at room temperature with the larger current. In the first experiment, solutions of sodium and cadmium nitrates were run for comparison. In the ammonium nitrate, the anode was covered with a black, slimy precipitate which was removed easily and left the surface darkened. No precipitate was formed because cadmium hydroxide is soluble in ammonium salts. The filtered electrolyte was strongly alkaline, a strong odor of ammonia was apparent and nitrite was formed in large quantities.

TABLE XXXVII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5407	0.9554	1 hr.	2.5
2	0.4083	0.7216	1 hr.	1.9
3	0.5373	0.9496	1 hr.	2.5
4	0.6134	1.084	1 hr.	2.8

Run	$NaNO_3$	$Cd(NO_3)_2$	NH_4NO_3
1	g. 1.3727_5 % 143.6	1.3523_1 141.5	2.2988_6 240.6 2.2224_4 232.6

Run	NH_4NO_3				
2	g. 1.8785_1 % 260.3	1.7497_2 242.5	1.7413_3 241.3	2.1890_4 303.4	1.5708_5 217.7
3	g. 2.4996_6 % 263.2	2.0223_2 213.0	1.9405_3 204.4	2.4107_4 253.9	1.7554_4 184.9
4	g. 2.2434_1 % 206.9	2.1455_2 197.9	2.2529_3 207.8	2.6590_4 245.3	2.3414_5 216.0

This large excess corrosion led to the suspicion that the ammonium nitrate itself had a marked corrosive action

on the cadmium. Therefore, some experiments were tried in which weighed test pieces were subjected, with constant stirring, to the action of ammonium nitrate (75 grams per liter). No current was used in this group of experiments. The results showed that cadmium dissolved very readily in the nitrate solution forming, according to Morin,[1] $Cd(NO_3)_2.H_2O.2NH_4NO_3.CdO(NH_3)_2$, a crystalline compound which is readily decomposed by water with the precipitation of cadmium oxide. The test piece was covered with a black, slimy mass similar to that which appeared on electrolysis, the solution became strongly alkaline, a strong odor of ammonia was noted and nitrite was again formed in large quantities. In short, the behavior was exactly analogous to the behavior on electrolysis. The results are given below.

TABLE XXXVIII

Chemical corrosion of cadmium in ammonium nitrate solution
(Anodes used as test pieces)

Run	Time	2	3	4	5	6
1	1 hr.	1.4704 g.	1.488 g.	1.2157	1.3389	1.7909
2	1 hr.	1.6043 g.	1.6686 g.	1.9339	1.6669	1.1310

The above table gives some idea of the amount of cadmium which dissolves in ammonium nitrate in an hour. If this loss is deducted from the total loss by corrosion during electrolysis, the true electrochemical loss will be rather small.

Other ammonium salts show a similar behavior but do not dissolve so much cadmium as the nitrate. The chemical corrosion in the ammonium salts (75 grams per liter) was as follows:

TABLE XXXIX

(Anodes used as test pieces)

Run	Time	NH_4Cl	$(NH_4)_2SO_4$	NH_4NO_3	$NH_4C_2H_3O_2$	$(NH_4)_2C_4H_4O_6$
1	24 hrs.	0.1055_2	0.1213_5	7.8882_2	0.1028_1	0.0857_3
2	12 hrs.	0.0634_3	0.0536_4	7.0914_5	0.0633_1	0.0550_2

In all the solutions except the nitrate, the test piece was

[1] *Tommasi: Electrochimie, 217.*

coated with a small amount of black or brown oxide which could be easily removed leaving the surface clean and bright. The appearance in the nitrate solution has already been described. In all the solutions except the nitrate, the corrosion in the 24-hour run was much greater than in the 12-hour. In the nitrate solution, the formation of the black oxide coating served to protect the test piece against further corrosion and the amount dissolved in the longer run was not much greater than that dissolved in the shorter.

Some experiments were also made using solutions of cadmium and sodium nitrates acidified with various amounts of nitric acid (25 cc HNO_3 1.4 sp. gr. per liter) to see if the gray compound was formed in acid solutions. It was found only in the sodium nitrate solution containing 50 cc of acid. For comparison, runs were also made in nitric acid of this concentration. The high current efficiency was due to chemical corrosion aiding the electrochemical as shown by the fact that in 1 hour, 2.9146 grams of cadmium was dissolved in nitric acid of this concentration. If this amount is deducted from the loss during electrolysis, the current efficiency in nitric acid in run 1 is only 42.85 percent. The results with nitric acid in the two runs are not strictly comparable because the time was not the same. The results at room temperature with the larger current are given in the following table.

TABLE XL

Run	Cathode coulometer	100 percent Cd	Time	C D. amp/dm²
1	0.5138	0.908	1 hr.	2.4
2	0.4293	0.7587	3/4 hr.	2.7

Run	$Cd(NO_3)_2$ 150 cc HNO_3 50 cc	$Cd(NO_3)_2$ 100 cc HNO_3 100 cc	$NaNO_3$ 150 cc HNO_3 50 cc	$NaNO_3$ 100 cc HNO_3 100 cc	HNO_3 200 cc
1	g. 1.4543_2	2.0445_3	1.4906_4	1.888_1	3.2948_5
	% 160.2	225.2	164.1	207.9	362.9
2	g. 1.195_2	1.1830_3	1.1390_5	1.1774_1	1.7188_4
	% 147.5	155.9	150.1	155.2	226.5

In the electrolysis of the nitrate solutions, nitrite was always formed. There was a possibility that in the nitrate solution the corrosion might be greater than in the nitrate or that the nitrite might itself have a marked solvent action on the metal. The latter conjecture, however, will not explain the excess corrosion because only 0.0088 g of cadmium was dissolved chemically by sodium nitrite in an hour. A run was made using sodium nitrite (75 grams per liter) as electrolyte. At the conclusion of the run, the anodes were found to be covered with a white coating under which some black non-adherent oxide was formed. After these had been removed, the surface was fairly clean. A white precipitate was formed, the filtered supernatant liquid was alkaline, and a faint odor of ammonia was noted. The larger current was used and the experiment was carried on at room temperature.

TABLE XLI—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5533	0.9778	1 hr.	2.6

Run	$NaNO_2$				
1	g. 0.9915_1 % 101.4	0.9923_2 101.5	0.998_3 102.0	0.9975_5 102.0	0.9915_6 101.4

The corrosion was very much less than with the nitrate so the formation of nitrite will not account for the excess corrosion.

With copper, it is easy to account for any excess corrosion since we know that there is always a tendency for copper to dissolve as the cuprous salt. If cadmium and tin formed compounds with a valence of one, it would be easy to account for this excess corrosion. As stated before, no reference to tin with a valence of one could be found. However, it is known that cadmium sometimes forms compounds in which the valence is less than two. Marchand[1] found on heating

[1] Marchand: Pogg. Ann., 38, 145 (1836).

cadmium oxalate in a closed vessel that a green powder, which he thought was Cd_2O, was formed. Souchay and Lenssen[1] thought that this was not a compound but a mixture of cadmium and cadmium oxide although Marchand was unable to extract any cadmium by shaking with mercury. Morse and Jones[2] described a compound Cd_4Cl_7 which was made by heating metallic cadmium with cadmium chloride in an atmosphere of nitrogen. They also describe the preparation of Cd_4Br_7 and $Cd_{19}I_{23}$. When these compounds are treated with water, a grayish white, amorphous precipitate which was supposed to be CdOH is formed. It was impossible to isolate this compound because of its instability. Canzoneri[3] heated metallic cadmium and cadmium chloride together with the hope of obtaining a subchloride of cadmium, CdCl, which should be analogous to mercurous chloride since cadmium and mercury are in the same group of the periodic table. He obtained a lead-gray powder the composition of which depended on the relative amounts of cadmium and cadmium chloride used. If the chloride was in excess the gray powder had the composition $2CdO.CdCl_2$. On fusing cadmium oxide and chloride, a heavy white compound of the same composition was formed with evolution of heat. If the metal was in excess, the product contained relatively more cadmium than required for the composition $2CdO.CdCl_2$. This gray compound was insoluble in water but was decomposed by it into metallic cadmium and cadmium chloride. The products of the decomposition depend on the temperature and the proportions of substances used in its preparation. Tanatar[4], on heating cadmium oxalate in a stream of dry carbon dioxide, obtained a green, amorphous powder which has the composition Cd_4O. Tanatar and Levin[5], on heating equal parts of cadmium hydroxide and

[1] Souchay and Lenssen: Liebig's Ann., 103, 314 (1857).
[2] Morse and Jones: Am. Chem. Jour., 12, 488 (1890).
[3] Canzoneri: Gazz. chim. ital., 27, 486 (1897).
[4] Tanatar: Zeit. anorg. Chem., 27, 432 (1901).
[5] Tanatar and Levin: Centralblatt., 1902, II, 564.

cadmium oxalate in the presence of water up to 130°–140°, obtained a green powder which they believed to be Cd_3O_2. The same workers, on heating two parts of the oxalate with one part of the hydroxide under the same conditions as before, obtained another green powder which they believed had the composition Cd_2O and which on heating with water or out of contact with air gave metallic cadmium and cadmium oxide. Tanatar also showed that the heat evolved on treating gram molecular quantities of these oxides with dilute acids was less than that evolved on treating a gram molecule of cadmium oxide with acids of the same concentration. Denham[1] showed that cadmium was dissolved by cadmium sulphate in the warm limb of the "circulation apparatus" and deposited in the cold arm. Apparently the cadmium behaves like copper and forms a cadmous sulphate which is unstable at low temperatures, and breaks down, giving metallic cadmium and cadmium sulphate. The equation may be represented as follows

$$Cd + CdSO_4 \rightleftarrows Cd_2SO_4.$$

All this seems to indicate that cadmium with a valence of one is fairly authentic.

The possible analogy between copper and cadmium suggested by Denham's experiments made it possible that when cadmium was made anode in a 30 percent solution of sulphuric acid and the solution electrolyzed, using a high current density, it would behave as copper did under the same conditions. Fischer[2] showed that when copper wire was made anode in "best conducting sulphuric acid," *i. e.*, sulphuric acid of the above concentration, a high anode current density caused the formation of a cloud of pulverulent metallic copper which came from the decomposition of the cuprous sulphate formed at the anode. On repeating this experiment with cadmium, no pulverulent metallic cloud was formed but the cadmium dissolved leaving a very smooth, polished surface.

[1] Denham: Loc. cit.

[2] Fischer: Zeit. phys. Chem., 48, 177 (1904).

However, the experiment was tried by simply duplicating the conditions in the copper experiment. There is a possibility that, under proper conditions of acid concentration and anode current density, the metallic cadmium might be formed but there is at present no experimental data to prove or disprove this conjecture.

The compound which formed on the anode was grayish white and heavier than the ordinary cadmium hydroxide which could be "floated off" by water. No metallic cadmium could be separated from it by shaking with mercury and it dissolved in hydrochloric acid without evolution of gas, which was another indication that no uncombined metal was present in the substance. It was, however, impossible to prove the composition of the substance because it was unstable and broke down easily. And it would be difficult to obtain by electrolysis a sample of the substance which was entirely free from the cadmic hydroxide. But when the fact is taken into account that mercury, which is the closest chemical analogue of cadmium has two oxides Hg_2O and HgO, it is reasonable to suppose that cadmium should also have two oxides similar in constitution to those of mercury.

Denham has shown that heat favors the formation of the cadmous compound. Therefore, the effect of electrolyzing nitrate solutions heated to 95° was tried. The results were much the same as when the electrolysis was run at room temperature except that the gray substance did not adhere to the electrode but fell off and collected at the bottom of the cell. Nitrite was formed, spongy metal was deposited at the cathode and the filtered supernatant liquid was alkaline. The results are given in the following table and show that the corrosion efficiency was increased by increasing the temperature.

TABLE XLII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.6861	1.0358	1 hr.	2.7
2	0.6258	1.1059	1 hr.	2.9

Run	$NaNO_3$ — 95°			
1	g. 1.5369_1	1.5313_2	1.4906_3	1.541_4
	% 148.4	147.8	143.9	148.7
2	g. 1.6676_1	1.6539_5	1.6393	1.7446_4
	% 150.8	149.5	148.2	157.8

The effect which a change of current density has on the corrosion efficiency in nitrate solutions at room temperature was next tried. The results are given in the next table.

TABLE XLIII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.1057	0.1868	1 hr.	0.49
2	0.1177	0.2081	1 hr.	0.55
3	0.1311	0.2317	1 hr.	0.61
4	0.2618	0.4627	1 hr.	1.2
5	0.2415	0.4268	1 hr.	1.1
6	0.4745	0.8386	1 hr.	2.2
7	1.5048	2.6594	1 hr.	7.0
8	2.7497	4.8595	1 hr.	12.8
9	2.7465	4.8538	1 hr.	12.8

Run	$NaNO_3$				
1	g. 0.2289_1	0.2212_2	0.2345_3	0.2236_4	0.2347_5
	% 122.5	118.4	125.5	119.6	125.6
2	g. 0.2432_1	0.2401_2	0.2449_3	0.2519_4	0.2519_6
	% 116.9	115.4	117.7	121.1	121.1
3	g. 0.2937_1	0.2819_2	0.2923_3	0.2975_4	0.2936_5
	% 126.8	121.6	126.2	128.4	126.7
4	g. 0.6557_1	0.6617_2	0.6807_3	0.6753_4	0.6736_5
	% 141.7	143.0	147.1	146.0	145.6
5	g. 0.5903_1	0.6146_2	0.6038_3	0.608_6	0.6135_5
	% 138.2	144.0	141.1	142.4	143.7
6	g. 1.1722_6	1.1799_7	1.1752_8	1.1949_9	1.1959_{10}
	% 139.8	140.8	140.1	142.5	140.2
7	g. 4.3706_6	4.2952_7	4.2743_8	4.4252_9	4.3398_{10}
	% 164.3	161.5	160.7	166.4	163.2
8	g. 8.4377_6	8.4005_7	8.3672_8	8.4398_9	8.4860_{10}
	% 173.6	172.9	172.2	173.7	174.6
9	g. 8.244_6	8.3920_7	8.2297_8	8.2934_9	8.3952_{10}
	% 169.9	172.9	169.6	170.9	173.0

These results show that the corrosion is markedly increased by increasing the current density. This means, no doubt, that a high current density at the anode favors the formation of the cadmous compound.

Attention has been called to the fact that nitrite was always formed when a solution of nitrate was electrolyzed. The greater part of the nitrite will, of course, come from cathodic reduction. The questions arose as to whether any nitrite was formed by the reaction which took place at the anode, especially since the cadmous compounds are said to possess marked reducing power and furthermore, whether an alkali was necessary for the formation of the gray oxide. The experiments with cadmium nitrate indicated that the presence of an alkali was not necessary to bring about its precipitation. To answer these questions, some experiments were tried with the anode and cathode compartments separated by a porous cup. The cadmium anode in sodium nitrate was placed in the anode compartment and the platinum wire cathode in the cathode compartment. As cathode liquid several different solutions were used. First, sodium nitrate acidified with nitric acid was tried but the objections were that both sodium hydroxide and sodium nitrite would be formed in the cathode compartment and their anions would move to the anode. Then dilute nitric acid was tried and the solution was kept acid by constant addition of nitric acid during the electrolysis. While this overcame the first objection it did not overcome the second because the anions of nitrite, which was formed in the cathode compartment, would migrate into the anode compartment and it was one of the objects of the experiment to see if any nitrite was formed by the action of the gray oxide on sodium or cadmium nitrates. Furthermore, the nitric acid might diffuse into the anode compartment and attack the anode chemically. The nascent hydrogen thus liberated would have a marked reducing effect on the nitrate present. When these two solutions were used as cathode liquid, nitrite was found in the anode compartment and the gray substance was formed on

the anode. The corrosion efficiency in these runs was about the same as when the anode and cathode compartments were not separated. The results are given in the following table.

TABLE XLIV—CADMIUM

Run 1. Cathode in $NaNO_3$ acidified with HNO_3

Run 2. Cathode in dilute HNO_3—kept acid throughout the run.

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5245	0.9267	1 hr.	2.4
2	0.5133	0.9071	1 hr.	2.4

Run	$NaNO_3$			
1	g. 1.2997_1	1.3480_2	1.3152_3	1.3241_4
	% 140.3	145.5	141.9	142.9
2	g. 1.2839_1	1.2958_2	1.3185_3	1.2912_4
	% 141.5	142.8	145.4	142.3

The third solution which was used as a cathode liquid was a saturated solution of copper sulphate. With this solution in the cathode compartment, there will be no great danger of any nitrite being formed in large quantities by cathodic reduction of any nitrate which has diffused into the cathode compartment. Furthermore, any sodium hydroxide formed at the cathode will immediately react with the copper sulphate and cannot diffuse out into the anode compartment and precipitate the cadmium compounds which are formed at the anode. Under these conditions the gray oxide was again formed at the anode and there was also a large quantity of nitrite formed in the anode compartment while none was found in the cathode compartment. The liquid in both compartments remained neutral. Several experiments were tried and the results could be duplicated every time. The results of one quantitative experiment are here given.

TABLE XLV—CADMIUM

Cathode in a saturated solution of $CuSO_4$

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5552	0.9812	1 hr.	2.6

Run	$NaNO_3$				
1	g. 1.4352_1	1.3521_2	1.5107_3	1.4317_4	1.4380_5
	% 146.2	137.8	153.9	145.9	146.3

The results indicated that the formation of this gray compound did cause a reduction of sodium nitrate to sodium nitrite.

Some experiments were tried under the same conditions with copper, tin, and zinc. Cadmium was also run for comparison. With copper, no precipitate except a small amount of cuprous oxide was formed. The anode solution became slightly acid to litmus and no nitrite was found. With zinc, a grayish white gelatinous hydroxide was formed on the anode but it was easily removed leaving the surface clean. The filtered anode liquid was slightly alkaline to litmus and gave a slight test for nitrite. With tin, a heavy white precipitate was formed and the anode was coated with the same gray substance as formed when the electrolysis was run without a cup. The anode, after this substance had been removed, was clean. The filtered anode liquid was slightly acid to litmus and contained no nitrite. The results with cadmium have already been described. In all cases, the copper sulphate in the porous cup remained neutral.

The results are given in the following table.

TABLE XLVI

Cathode in saturated solution of $CuSO_4$. Time one hour

Run	Cathode coulometer	Anode metal	100 percent corrosion	C. D. amp/dm²	$NaNO_3$
1	0.4057	Cd	0.717	1.9	g. 1.0248_2 % 142.9
		Cu	0.4057	1.9	g. 0.4203_3 % 103.6
		Sn	0.7601	2.2	g. 1.360_8 % 178.9
		Zn	0.4172	2.7	g. 0.4187_1 % 100.3
2	0.5932	Cd	1.0484	2.7	g. 1.3194_2 % 125.9
		Cu	0.5932	2.7	g. 0.6098_7 % 102.8
		Sn	1.1098	3.2	g. 1.926_6 % 173.5
		Zn	0.610	4.0	g. 0.5914_1 % 97.2

The efficiency of corrosion was about the same or perhaps a trifle less than when the anode and cathode are not separated by the cup.

In order to show whether or not nitrite was formed when metals were placed in nitrate solutions, zinc, copper, nickel, tin, iron and cadmium were placed in nitrate solutions which were free from nitrite and set aside for a week in beakers covered with cover glasses but to which air had free access. At the end of the week, zinc gave the best test for nitrites, cadmium a good test, iron only a fair test, while copper, nickel and tin gave no test at all. This experiment was repeated and the same results were obtained, indicating that the current was not necessary to bring about the reduction of nitrate to nitrite.

Summary

In this work, the electrolytic corrosion of zinc, copper, nickel, tin, iron and cadmium was studied in solutions of sodium chloride, sulphate, nitrate, acetate and tartrate containing 75 grams of salt per liter. The results showed that the

metals corroded to different extents in the different solutions, although some corroded to about the same extent in two and sometimes in three electrolytes. The corrosion was found in some cases to approximate closely to the theoretical amount, in others to be very much less and in still others to be very much greater than the theoretical. When the corrosion was less than theoretical, it was found that further electrolytic action was prevented by the formation of an oxide or hydroxide film on the anode. In some cases, notably copper and tin in the tartrate solution, the formation of this film caused a marked increase in the resistance of the circuit. When the corrosion was greater than theoretical, the excess corrosion was not due to any appreciable extent to loss of metal by mechanical disintegration, although there will always be some slight loss due to this cause but never enough to account for any large excess. The excess corrosion may then be due to the formation of compounds in which the valence is less than the lowest ordinary valence of the metal. It is known that there is always a tendency for copper to dissolve to some extent in the cuprous form and in cases where the corrosion was greater than theoretical with copper anodes the presence of some cuprous salts could always be shown. To explain the large excess corrosion of tin and cadmium in sodium nitrate solution the existence of "subvalent" forms of these metals (*i. e.*, valence of one) has been postulated.

The effect of changing the concentration from 75 to 25 grams per liter was tried and it was found that the differences in corrosion in the two solutions were in general very small. However, change of concentration of the tartrate solution did sometimes lead to precipitation with the more dilute solution whereas with the more concentrated no precipitate was formed. Any decrease in corrosion noted was due to the fact that the insoluble film was formed more quickly in the dilute solution or in other words the conditions for the metal becoming passive were improved.

The effect of decreasing the current density was also studied and the results showed that with some metals, the

corrosion in the same solution was increased by a decrease of the current density while with other metals, it was decreased and with still others, it was little affected one way or the other. On the other hand with cadmium in the sodium nitrate solution, it was found that the corrosion was markedly increased by increase of the current density.

Increase of temperature was also shown to have an effect on the corrosion of copper in some of the solutions although the formation of a heavy layer of cuprous oxide on the anodes in some of the solutions prevented a very pronounced increase. With cadmium in sodium nitrate solution, the corrosion was appreciably greater at the higher temperatures.

In nearly all solutions, the filtered supernatant liquid was alkaline after electrolysis and in some solutions metal was deposited at the cathode. This metal may come from reduction of the metallic hydroxides by the nascent hydrogen at the cathode or from the electrolytic decomposition of basic salts. In some cases, the amount of metal thus deposited was large.

The electrolyte and the precipitated hydroxide were subjected to the action of any gases which were liberated at the electrodes. Thus there will always be a tendency to reduction at the cathode and it was found that nitrite was always formed on the electrolysis of nitrates and that the quantity of nitrite formed, depended in some measure on the metal used as anode. Experiments were also tried to see how the nitrite affected the corrosion of the metal both chemically and electrochemically and it was found that the excess corrosion in the nitrate solution could not be accounted for by the action of the nitrite. On the other hand if the metal went passive, oxygen was liberated at the anode and the electrolyte was subjected to oxidation which might change its chemical nature and bring about further changes in the products of the electrolysis. Such a case was found when copper went passive in the tartrate solution and the tartrate was oxidized with the formation of formic acid which in

alkaline solution reduced the cupric compounds to cuprous hydroxide. Furthermore with a nickel anode, the solution was changed by oxidation to a dark brown liquid.

In some cases, excess corrosion may be explained by the solvent action of the electrolyte on the anode metal, the chemical corrosion working with the electrochemical to give a total loss which exceeds the theoretical.

A very important factor was the electrode surface and care was taken to file and scour each anode with carborundum paper before beginning the electrolysis to insure a new and clean surface for each run. Even then, it was impossible to duplicate the results exactly. Experiments with freshly deposited copper showed that there were discrepancies in the results even with this precaution to insure a uniform anode.

This work was suggested by Professor Bancroft and carried on under his supervision. This opportunity is taken to thank him for his kindly interest in the work and for the many fruitful suggestions he made during its progress.

Cornell University

NEW BOOKS

Das Schicksal der Planeten. *By Svante Arrhenius. 15 × 22 cm; 55 pp. Leipzig: Akademische Verlagsgesellschaft, 1911. Price: 1.50 marks.*—In this little pamphlet Arrhenius sketches the past, present and future states of the planets so far as they can be guessed at.

"In Iquitos on the Amazon the mean humidity is 83 percent. The annual temperature variation is only about 5° C.; in Para it is only 1.0°–1.5°. The diurnal variation is usually much greater. During the rainy season the sky is usually very clear between showers. Back from the coast in Guiana the rainy season lasts from the end of April till July or August. During the dry season there are heavy dews which keep things damp. The sun and the moon are rarely to be seen. Frightful thunder storms mark the beginning of the rainy period.

"If we increase these conditions of moisture and cloudiness very much, we get a climate such as presumably prevailed while the coal deposits were being formed. Such a climate now occurs on Venus: continuous cloudiness; a dripping wetness even in the dry season; no appreciable difference of temperature between the pole and the equator, between summer and winter, or between day and night, owing to the thick mantle of clouds; tremendous downpours of rain during the rainy season, presumably accompanied by violent thunderstorms."

"In consequence of the unchanging climate the animals and plants need and have no power of adapting themselves to different seasons. Cryptogams and lower animals alone occur and about the same kinds are found in all parts of the planet. Owing to the abundant food supply, giant forms are produced."

The conditions on Venus, according to Arrhenius, are thus an intensified form of those now prevailing on the Amazon. A study of the Turkestan deserts gives us a fair idea of what Mars is like, except that we must remember that the temperature there is much lower than on the earth, the mean temperature in the shade in midsummer being about —17° C. Under these conditions we have calcium chloride oceans whenever there is any water at all.

Arrhenius does not believe in the existence of canals on Mars (p. 43). "The south pole of Mars is surrounded by a large, dark-colored region in which some leather-colored spots appear as islands. This used to be considered an ocean; but Lowell has found darker lines or canals in it and, therefore, assumes that this is an enormous garden with irrigating ditches running through it. It was presumably once a polar sea; but for millions of years it has been covered with an ice crust at least a kilometer thick, frozen fast to the shore. The ice on our polar sea is covered with fresh-water pools in summer, which freeze in winter. In the same way pools tend to form on the polar sea of Mars in summer though the water is salt and not fresh." The damp places look dark. The water gathers in the deepest places which coincide with the faults due to earthquakes. On the earth the faults run in straight lines just as the canals do on Mars. It is also interesting that the river bed in one of the Turkestan deserts is about 15 kilometers in width, which is about the average width of the so-called canals on Mars.

Arrhenius concludes, p. 47, that "we do not need to assume any unknown forces or properties of matter in order to account for conditions on Mars. Everything takes place just as it would have on the earth if the temperature had been, for several geological periods, about 40° below its present mean. The earth will probably suffer the sombre fate of Mars when the sun begins to cool off a good deal more."

The general development of the planets is summed up by Arrhenius, p. 52, as follows:

"When the magma cools, a solid surface forms and only then can we speak of a special development of the atmosphere and of the interior of the planets. From inside the planets come gases, chiefly water vapor and carbon dioxide, which mount to the highest regions of the atmosphere. The sunlight causes photochemical reactions to take place in these highest regions, far above the clouds and above the newly formed atmosphere with its high absorbing power (a very strong absorption of light has been observed by Slipher in the outermost layers of Uranus and of Neptune). At the low temperatures prevailing in these higher layers the photochemical reactions are by far the most important because they are scarcely affected by the cold while ordinary chemical reactions, and especially those between gases, take place slowly at ordinary temperatures and are very much affected by a lowering of the temperature. Through these photochemical reactions and the ensuing chemical ones, carbon and oxygen are formed, a reaction now carried out by the catalytically active chlorophyll. The reducing gases of the original atmosphere, hydrogen, hydrocarbons, etc., are gradually removed by combustion with oxygen until finally, in addition to oxygen, there are left only chemically inert gases, such as nitrogen, as the chief constituents of the atmosphere. Through cracks in the planet's crust there escape into the air, water vapor and carbon dioxide, the two gases which with oxygen are essential to life. Without question, life develops on the surface of the planet under these conditions. This is the stage in which the earth is and probably Venus, though the development is less advanced there than on the earth owing to the higher mean temperature of about 65° C.

"Gradually the crust thickens. Water vapor condenses to form oceans. Carbon dioxide and, to some extent, water are taken up as the rocks weather and are deposited by crustacea as calcium carbonate. At the same time water washes sand and clay into the ocean, forming large layers of sedimentary rocks. Volcanic outbursts decrease gradually and consequently there is a decrease in the flow of water vapor and carbon dioxide from the interior of the planet. The amounts of these substances decrease as a result of the continued weathering. The surface of the planet becomes a desert. This is the stage in which Mars now is.

"Plant life ceases. No oxygen is formed and the existing oxygen combines to some extent with nitrogen to form nitrates while the balances oxidizes iron compounds. In time the free oxygen and nitrogen disappear. Owing to lack of water there is practically no circulation. The air becomes less dense and the temperature differences between day and night, winter and summer become greater. The last gases disappear with the molecular motion. This is the stage in which the moon now is, probably also Mercury and most of the

moons of the other planets. From now on the celestial body is dead and unchangeable." *Wilder D. Bancroft*

The Cyanide Handbook. *By J. E. Clennell. 16 × 24 cm; pp. xi + 520 pp. New York: McGraw-Hill Book Company, 1910. Price: $5.00 net.*— In the introduction the author says that "notwithstanding the fact that so much has been written about the cyanide process since its successful establishment in South Africa in 1890, there still appear to be some aspects of the subject which are only slightly touched upon, or quite inadequately treated, by the many able exponents of the process, and many facts of great value to the practical workers can only be gathered by long and painful search through technical literature."

"The aim of the present work is to bring together such scattered information in a handy and accessible form, which will appeal to all workers interested in the process, whether as managers of plants, foremen, chemists or assayers. Depending, as it does, on the application of chemical principles, a very important section of the work connected with a cyanide plant is carried on in the laboratory; this department will therefore receive a larger share of attention than is usually given to it in books of this description."

The book is divided into nine parts entitled: general; chemistry; preparatory treatment of ore for cyaniding; the dissolving process; the precipitation and smelting process; special modification of the cyanide process; assaying; analytical operations; metallurgical tests.

The book is well written, seems to be thorough, and should be of value to the technical man. There are also many matters in it, which are of interest to the chemists who are not connected with the industry. The fact that cyanide or sodium prevents the flouring of mercury, pp. 17, 184, is of distinct interest in its bearing on the behavior of colloids. One would like to know, pp. 119, 254, why "when solutions pass 1.5 ounces gold per ton, the gold on the shavings assumes a yellow color, and passing two ounces and upward is usually golden yellow in the first compartment shading off in the following compartments to the usual black-colored deposit obtained from poor solutions." It is not clear, p. 181, why "plates previously amalgamated with gold or silver are more effective in catching the precious metals than copper plates amalgamated only with pure mercury." The theory of the flotation process, p. 192, is still in a very rudimentary stage. We have still something to learn about the theory of the lead-zinc couple, p. 246, and we do not know at all why certain "foul" solutions, p. 299, cause good precipitation of gold or zinc. According to the author, p. 256, it is still an open question what becomes of all the zinc that is corroded. It is very interesting to note, p. 283, the rate at which gold is dissolved from finely crushed ore.

When discussing the fact, p. 105, that there is an optimum concentration of potassium cyanide, the author makes the mistake of assuming that the concentration of cyanide as ion is greater in dilute solutions; because the salt is more completely dissociated. The percentage dissociation is greater in dilute solutions; but the absolute concentration of cyanide as ion is highest in the concentrated solutions. It is probable, as suggested, that the solubility of the oxygen is an important factor. *Wilder D. Bancroft*

Die neue Welt der flüssigen Kristalle *und deren Bedeutung für Physik, Chemie, Technik und Biologie. By O. Lehmann. 17 × 24 cm; pp. vi + 388. Leipzig: Akademische Verlagsgesellschaft, 1911. Price: 12 marks.*—The headings of some of the chapters are as follows: What is a crystal; how is anisotropism to be explained; what does a crystal do when bent; is an amorphous mass formed by grinding; crystals and living organisms; the discovery of the inversion temperature; double saturation and the disappearance of a solid phase; the three states of matter; what are amorphous substances; amorphous substances are not phases; are there really plastic crystals; are there also liquid crystals; physically homogeneous, crystalline liquids; optical properties of thick liquid crystals; substances with several liquid states; how do myeline forms occur; apparently living crystals; growth of a living organism; latent life and soul; the soul of an atom; self-purification of liquid crystals; liquid crystals and magnetism.

These are interesting titles and the book itself is interesting. More than that one cannot say. The author deals, in many cases, with matters involving the principles of physical chemistry but he does not apply these principles as others do. On p. 87 he deduces that two modifications of ammonium nitrate must exist as such in solution because the solution may be supersaturated with respect to both forms. He fails to point out that there is no other evidence of the existence of two liquid forms, and that when we do have evidence of two liquid modifications in the solution it is not necessarily the less soluble which is the more stable. In fact he states definitely, p. 93, that the less stable modification is the more soluble and has the lower melting point. He also considers that water vapor for instance contains ice vapor as such. This may be true but it has not been proved nor has the usefulness of the hypothesis been demonstrated. Few will agree that there are substances, p. 141, without any vapor pressure and not many will agree with his definition of a phase, p. 133. It is quite incorrect to say, p. 364, that the phase rule does not apply to liquid crystals; the quotation from Ostwald does not mean what the author implies and is merely a reason for considering liquid crystals as a solid phase.

Another reason why the book is not so helpful as it should be is that the author is much too dramatic. He is continually trying to impress people with the extraordinary and mysterious nature of the liquid crystals. The book gains in interest by this treatment but loses in value. All that is necessary to make everything fall into line is to say that flowing (*fliessende*) crystals are crystals in which the surface tension is strong enough to round off the corners, while liquid (*flüssige*) crystals are ones in which the surface tension is sufficiently strong to produce a sphere. No further assumption is necessary in order to explain all the experimental data; but if one started that way, it would not be possible to write many books on liquid crystals and one could not discuss their significance with respect to physics, chemistry and biology because there would not be any. On the other hand, we should have lost a very interesting book.

Wilder D. Bancroft

THE ELECTROLYTIC REDUCTION OF NITROBENZENE

BY RALPH CUTHBERT SNOWDON

One would naturally expect that the chemical and the electrochemical methods of reducing nitrobenzene would run fairly parallel and that a method which worked well in one case would at least be tried in the other way. The development has not proceeded along these lines, the chemical and the electrochemical methods being rather surprisingly different in most cases. This is an unfortunate condition. It will take a great deal of work to fill in the gaps in our knowledge, and the first thing to do is to call attention to these gaps, I shall therefore give an outline of some of the more interesting chemical methods of reduction and then of the electrochemical methods.

Nitrosobenzene

Since nitrosobenzene is more readily reduced than nitrobenzene,[1] it has not been possible to prepare it by direct reduction of nitrobenzene. It was prepared by Baeyer[2] in 1874 by the action of nitrosyl bromide on mercury phenyl in benzene solution,

$$Hg(C_6H_5)_2 + NOBr = C_6H_5HgBr + C_6H_5NO.$$

Baeyer did not isolate the compound and this was first accomplished in Bamberger's laboratory nearly twenty years[3] later. Bamberger obtained it by oxidation of diazobenzene with alkaline potassium ferricyanide or potassium permanganate. It can be made by the action of cold chromic acid mixture, or by the action of almost any oxidizing agent, on phenylhydroxylamine. Nitrobenzene can also be made by oxidizing aniline with potassium permanganate,[4] with Caro's

[1] Haber: Zeit. Elektrochemie, 4, 509 (1898).

[2] Ber. chem. Ges. Berlin, 7, 1638 (1874).

[3] Bamberger: Ber. chem. Ges. Berlin, 26, 472, 482 (1893); 27, 1182, 1273, 1374, 1555 (1894).

[4] Bamberger and Tschirner: Ber. chem. Ges. Berlin, 31, 1524 (1898).

acid,[1] peroxide, etc.; but the reaction goes through the phenylhydroxylamine stage. Quite recently Oddo[2] has brought out a modification of the original Baeyer method, letting nitrosyl chloride react with phenyl magnesium bromide,

$$C_6H_5MgBr + NOCl = C_6H_5NO + MgBrCl.$$

Nitrosobenzene forms colorless crystals, melting at 68° to a green liquid. The alcoholic and ethereal solutions are also green. The substance is very volatile. It is easily oxidized to nitrobenzene and easily reduced to phenylhydroxylamine. In an alkaline, alcoholic solution[3] nitrosobenzene reacts rapidly with phenylhydroxylamine, forming azoxybenzene,

$$C_6H_5NO + C_6H_5NHOH = C_6HN\begin{matrix}O\\ \diagup\ \diagdown\end{matrix}NC_6H_5 + H_2O.$$

It reacts with hydrazobenzene[4] to form azobenzene, and phenylhydroxylamine, the phenylhydroxylamine of course reacting with nitrosobenzene to form azoxybenzene in case the solution is alkaline,

$$C_6H_5NO + C_6H_5NH.HNC_6H_5 = C_6H_5N : NC_6H_5 + C_6H_5NHOH.$$

Azobenzene is also formed by the reaction between nitrosobenzene and aniline[5] in acetic acid solution,

$$C_6H_5NO + C_6H_5NH_2 = C_6H_5N : NC_6H_5 + H_2O.$$

It seems probable that aniline is first oxidized to hydrazobenzene, but we do not know this. Nitrosobenzene reacts with hydroxylamine to form syndiazobenzene,[6]

$$C_6H_5NO + NH_2OH = C_6H_5N_2OH + H_2O.$$

Nitrosobenzene in benzene solution is decomposed by light,[7]

[1] Caro: Zeit. angew. Chem., 1898, 845.
[2] Gazz. chim. ital., 39 I, 659 (1908).
[3] Bamberger: Ber. chem. Ges. Berlin, 30, 2278 (1897); Haber: Zeit. Elektrochemie, 4, 509 (1898).
[4] Haber: Zeit. phys. Chem., 32, 280 (1900).
[5] Baeyer: Ber. chem. Ges. Berlin, 7, 1639 (1874).
[6] Hantzsch: Ber. chem. Ges. Berlin, 38, 2056 (1905).
[7] Bamberger: Ber. chem. Ges. Berlin, 35, 1606 (1902).

azoxybenzene being the chief, but by no means the only product.

Phenylhydroxylamine

Phenylhydroxylamine can be prepared by reducing nitrobenzene with zinc, zinc dust[1] or zinc amalgam and water. The reaction takes place more rapidly and more satisfactorily in presence of calcium chloride or ammonium chloride.[2] Bamberger and Knecht[3] use aqueous alcohol instead of water, and aluminum sulphate as the electrolyte. The lower the temperature, the less the danger of the phenylhydroxylamine decomposing.

When nitrobenzene reacts with hydrazobenzene, the intermediate stages in the reduction are nitrosobenzene and phenylhydroxylamine, but this is not a satisfactory method of making phenylhydroxylamine. When aniline is oxidized by permanganate, Caro's acid, etc., phenylhydroxylamine can be detected under suitable conditions as one of the oxidation products.

Phenylhydroxylamine forms colorless crystals melting at 81°. It is easily oxidized to nitrosobenzene[4] and is easily reduced to aniline. It reduces ammoniacal silver solutions and Fehling's solution in the cold. In strongly acid solutions phenylhydroxylamine changes into *p*-aminophenol.[5] When air is excluded from the alkaline solution, a simultaneous oxidation and reduction takes place with the formation of nitrosobenzene and aniline,

$$2C_6H_5NHOH = C_6H_5NO + C_6H_5NH_2 + H_2O.$$

The nitrosobenzene[6] so formed reacts with unchanged phenylhydroxylamine to give azoxybenzene,

$$C_6H_5NHOH + C_6H_5NO = C_6H_5\overset{O}{\overset{\diagup\diagdown}{N}}NC_6H_5 + H_2O.$$

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[1] Bamberger: Ber. chem. Ges. Berlin, 27, 1348 (1894).
[2] Wohl: Ber. chem. Ges. Berlin, 27, 1432 (1894).
[3] Ibid., 29, 863 (1896).
[4] Bamberger: Ber. chem. Ges. Berlin, 27, 1349 (1896).
[5] Friedländer: Ber. chem. Ges. Berlin, 26, 177 (1893).
[6] Quoted from Sidgwick: "Organic Chemistry of Nitrogen," 98 (1910).

"If the air is not excluded, the solution rapidly absorbs oxygen. If the (neutral) aqueous solution is exposed to the air the body is oxidized to nitrosobenzene. At the same time, for each molecule of nitrosobenzene formed, one molecule of hydrogen peroxide is produced. That is to say, in this, as in the other 'autoxidations,' for whatever reason, one-half of the oxygen goes to the substance oxidized, and the other half combines with the water.

"The alkaline solution[1] is much more easily oxidized by the air, so easily that it can be used like pyrogallate for removing oxygen in gasometry.[2] In this case only traces of hydrogen peroxide can be detected, while much nitrobenzene is formed, the hydrogen peroxide being used up in the presence of the alkali to oxidize nitrosobenzene the primary product, to nitrobenzene." Thus in neutral solution (air present) we have the reactions

$$C_6H_5NHOH + O_2 = C_6H_5NO + H_2O_2$$

$$C_6H_5NHOH + C_6H_5NO = C_6H_5N\overset{O}{<}NC_6H_5 + H_2O$$

while in alkaline solution (air present) we have

$$C_6H_5NHOH + C_6H_5NO = C_6H_5NHOH + O_2 =$$
$$C_6H_5NO + H_2O_2 = C_6H_5NO_2 + H_2O.$$

In alkaline solutions there is a slight tendency for phenylhydroxylamine to change into azobenzene.[3]

Nitrous acid converts phenylhydroxylamine into phenylnitrosohydroxylamine,[4] $C_6H_5N(NO)OH$, which does not even reduce a boiling Fehling's solution and which is quite stable in presence of alkalies, acting like a strong acid, forming neutral salts which are not decomposed by carbonic acid. Mineral acids change the substance readily into nitrosobenzene and other products.

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[1] Bamberger: Ber. chem. Ges. Berlin, 33, 113 (1900).

[2] Bamberger and Brady: Ber. chem. Ges. Berlin, 33, 271 (1900).

[3] Cf. Haber: Zeit. phys. Chem., 32, 279 (1900). Löb: Ibid., 34, 664 (1900).

[4] Meyer and Jacobsen: Lehrbuch der organischen Chemie, 2, 245 (1902).

Azoxybenzene

A quantitative yield of azoxybenzene can be obtained by heating nitrobenzene together with a solution of sodium methylate in methyl alcohol.[1] The reaction appears to be,

$$4C_6H_5NO_2 + 3CH_3ONa = 2C_6H_5N\overset{O}{\diagup\diagdown}NC_6H_5 + 3HCO_2Na + 3H_2O.$$

Since Klinger's methyl alcohol was not free from water, it occurred to Lachmann[2] that the reaction would probably take place just as well with a methyl alcohol solution of caustic soda. This proved to be the case and Lachmann obtained a 97 percent yield by boiling for three hours. It is important that there should be no acetone in the methyl alcohol and it is possible that presence of acetone was the reason that Moltschanowsky[3] was unable to duplicate Klinger's results. The reaction should probably be written

$$4C_6H_5NO_2 + 3CH_3OH + 3NaOH =$$

$$2C_6H_5N\overset{O}{\diagup\diagdown}NC_6H_5 + 3HCO_2Na + 6H_2O.$$

The reduction of nitro compounds by alcoholic potash has been studied by Rotarski, but there seems to be something wrong in the statement of his results.[4] According to the review Rotarski found that the reaction at low temperature was

$$>O + CH_3ONa = NaOH + HCHO,$$

while at high temperature it was

$$>O + CH_3ONa = HCO_2Na + H_2.$$

It was also found that aldehydes did not reduce the nitro compounds even in alkaline solutions. From this Rotarski concludes that hydrogen compounds, such as hydrazobenzene or aniline, will be formed at low temperatures while deoxidized

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[1] Klinger: Ber. chem. Ges. Berlin, 15, 865 (1882).
[2] Jour. Am. Chem. Soc., 24, 1180 (1902).
[3] Jour. russ. phys. chem. Ges., 14, 224 (1882).
[4] Rotarski: Chem. Centralblatt, [5] 9, II, 893 (1905).

compounds, such as azoxybenzene or azobenzene, will be formed at high temperatures. The conclusion is correct as a matter of fact but it does not follow from the equations. Sidgwick[1] quotes from the same source, but leaves the matter quite as obscure as before. "Where alcoholic potash or sodium methylate is used as the reducing agent, its action depends on the temperature employed. At low temperatures the alcohol is oxidized to aldehyde, giving up two atoms of hydrogen. At higher temperatures sodium formate is produced: this implies that the alcohol takes up oxygen, but does not give off hydrogen:

$$CH_3OH + 2O = HCO_2H + H_2O.$$

Hence at high temperatures the hydrogenized compounds, such as the hydrazo and amine, are not produced, but only those compounds which are formed from the nitro by loss of oxygen alone, such as the azoxy and the azo."

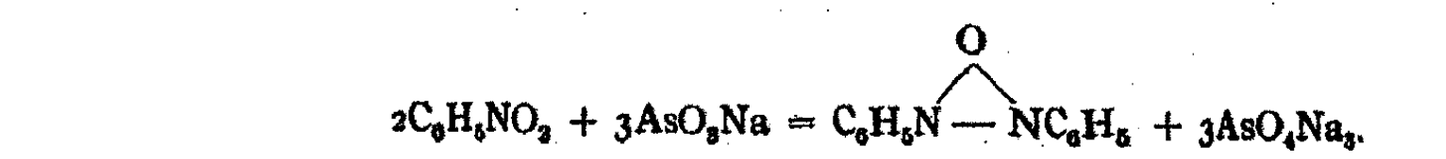
Azoxybenzene can be prepared by the action of sodium amalgam on an alcoholic solution,[2] the solution being kept nearly neutral with acetic acid. It is not easy to check the reaction at the proper stage but Moltschanowsky[3] reports an 87 percent yield of azoxybenzene. By regulating the quantities taken Heumann[4] was able to stop at the azoxy stage when using zinc dust and dilute aqueous caustic soda or ammonia.

Dechen[5] obtained a mixture of azoxybenzene and aniline with zinc dust and solutions of calcium chloride or sodium chloride at 105°–110°. The reduction is undoubtedly to phenylhydroxylamine which then decomposes, as previously stated, according to the equation,

$$3CHNHOH = C_6H_5NH_2 + C_6H_5N\overset{O}{\diagup\diagdown}NC_6H_5 + 2H_2O.$$

[1] "Organic Chemistry of Nitrogen," 156 (1910).
[2] Alexejew: Bull. Soc. chim. Paris, 1, 324 (1864).
[3] Jour. russ. phys. chem. Ges., 14, 225, 350 (1882).
[4] "Ladenburg's Handwörterbuch der Chemie," 2, 122 (1884).
[5] Ber. chem. Ges. Berlin, 21, 678 (1888).

Loessner[1] obtained a 70 percent yield of azoxybenzene by boiling nitrobenzene with a sodium arsenite solution,



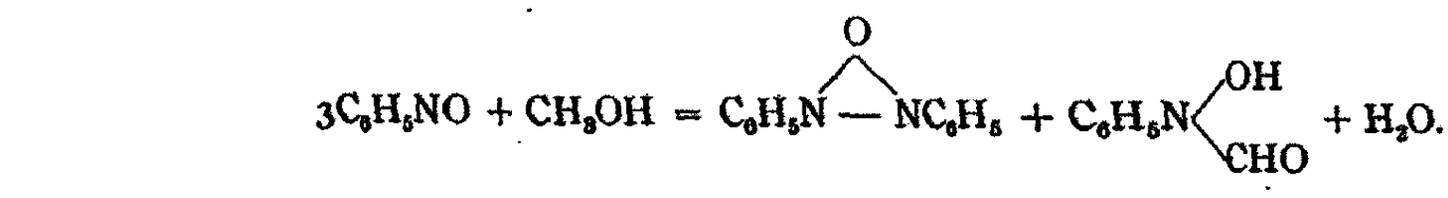
$$2C_6H_5NO_2 + 3AsO_3Na = C_6H_5N\langle O \rangle NC_6H_5 + 3AsO_4Na_3.$$

According to a German patent[2] azoxybenzene can be made by heating nitrobenzene and iron in caustic soda solution.

A quantitative yield of azoxybenzene is obtained when nitrosobenzene and phenylhydroxylamine react[3]

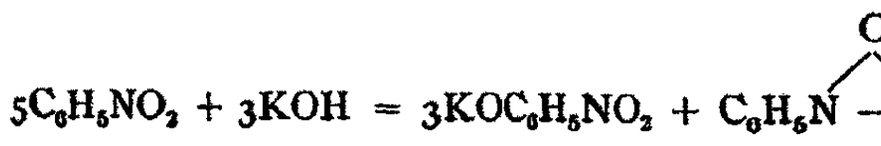
$$C_6H_5NO + C_6H_5NHOH = C_6H_5N\langle O \rangle NC_6H_5 + H_2O.$$

At room temperature, nitrosobenzene reacts with methyl alcohol in presence of caustic potash[4] forming azoxybenzene and formyl phenylhydroxylamine,



$$3C_6H_5NO + CH_3OH = C_6H_5N\langle O \rangle NC_6H_5 + C_6H_5N\langle \begin{matrix} OH \\ CHO \end{matrix} + H_2O.$$

According to Wohl and Aue,[5] nitrobenzene reacts with dry caustic potash, yielding *o*-nitrophenol and azoxybenzene,



$$5C_6H_5NO_2 + 3KOH = 3KOC_6H_5NO_2 + C_6H_5N\langle O \rangle NC_6H_5 + 3H_2O.$$

Azoxybenzene is one of the products when aniline hydrochloride is oxidized by permanganate and it can also be obtained by oxidizing azobenzene with an acetic acid solution of chromic acid.[6] Azoxybenzene forms pale yellow crystals melting at 36°. In solution it reduces direct to hydrazobenzene and not to azobenzene. When distilled slowly over

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[1] Jour. prakt. Chem., [2] 50, 564 (1894).
[2] Chem. Centralblatt, [5] 7, 372 (1903).
[3] Bamberger and Renauld: Ber. chem. Ges. Berlin, 30, 2278 (1897).
[4] Bamberger: Ber. chem. Ges. Berlin, 35, 732 (1902).
[5] Ber. chem. Ges. Berlin, 34, 2444 (1901).
[6] Petriew: Ber. chem. Ges. Berlin, 6, 557 (1873).

iron filings, azobenzene is formed.[1] Wallach[2] found that hot concentrated sulphuric acid changes azoxybenzene into *p*-hydroxyazobenzene, azobenzene also being formed.

Lachmann[3] says in regard to this:

"In view of the importance of properly understanding intramolecular rearrangements, I devoted much time to a study of the mechanism of this reaction, varying the experimental conditions within wide limits. No intermediate compounds between azoxybenzene and hydroxyazobenzene could be discovered. When azoxybenzene and sulphuric acid are mixed, a dark red solution is formed, with slight evolution of heat. If the mixture is poured into water azoxybenzene is recovered quantitatively. If allowed to stand in the cold for varying periods of time, the rearrangement proceeds slowly and is not complete after a week. If warmed in the water bath the reaction proceeds with greater or less velocity, depending upon so many factors that it seems hopeless to find any relationship between them. But in all cases, much the same products are formed in varying amounts, and with more or less unchanged azoxybenzene if the process be interrupted before completion."

Lachmann came to the conclusion that the azoxybenzene was formed by auto-reduction of the hydroxyazobenzene,

$$n(C_6H_5N : NC_6H_5OH) = (n - x)C_6H_5N : NC_6H_5 + [xC_6H_5N : NC_6H_4OH(n - x)O],$$

where n is a large number and x a small one.

Azoxybenzene reacts very slowly with hydroxylamine.[4] When boiled for six hours with free hydroxylamine in a methyl alcohol solution containing a large excess of caustic potash, there was almost no reduction. When the same solution was heated for sixteen hours in a pressure flask at 100° a 90 percent yield of azobenzene was obtained.

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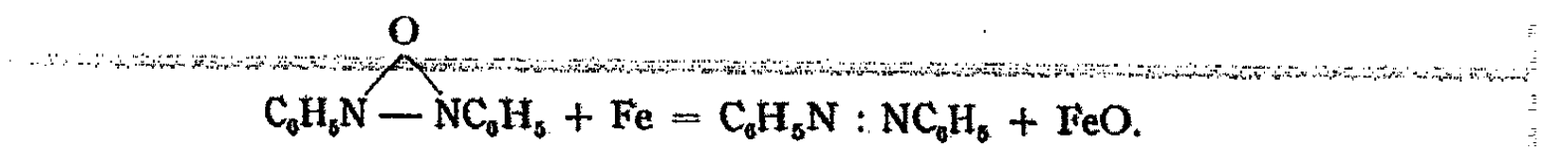
[1] Schmidt and Schultz: Liebig's Ann., 207, 328 (1881).
[2] Ber. chem. Ges. Berlin, 13, 525 (1880); 14, 2617 (1881).
[3] Jour. Am. Chem. Soc., 24, 1181 (1902).
[4] Lachman: Jour. Am. Chem. Soc., 24, 1193 (1902).

Azobenzene

Mitscherlich[1] prepared azobenzene by heating nitrobenzene with alcoholic potash and then distilling. Zinin[2] showed that the reduction was to azoxybenzene which decomposed when distilled. Rasenack[3] recommends adding sodium chloride to azoxybenzene before distilling it because there is less charring under these conditions. A more satisfactory way of converting azoxybenzene into azobenzene is to heat with iron filings.[4]



$$C_6H_5N\langle O \rangle NC_6H_5 + Fe = C_6H_5N : NC_6H_5 + FeO.$$

Azobenzene can be made by the action of sodium amalgam and acetic acid on alcoholic nitrobenzene.[5] Rasenack[6] recommends dissolving nitrobenzene in wet ether, and reducing with sodium amalgam. Azobenzene can also be formed by the action of zinc and caustic soda on alcoholic nitrobenzene; but the reaction is apt to run to the hydrazo stage in which case azobenzene is obtained by oxidizing the hydrazobenzene. The method appears to work well with alkyl-substituted nitrobenzenes.[7] Mixter[8] obtained azobenzene and hydrazobenzene by the action of platinized zinc on nitrobenzene dissolved in alcoholic ammonia. We do not need to go into the question whether reduction with platinized zinc is to be classified as chemical or electrochemical. The case is cited because the azobenzene was probably an oxidation product of hydrazobenzene.

According to a German patent[9] azobenzene can be made from nitrobenzene or azoxybenzene by suitable heating with

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[1] Liebig's Ann., 12, 311 (1834).
[2] Jour. prakt. Chem., 36, 93 (1845).
[3] Ber. chem. Ges. Berlin, 5, 367 (1872).
[4] Schmidt and Schultz: Liebig's Ann., 207, 329 (1881).
[5] Alexejew: Bull. Soc. chim. Paris, [2] 1, 324 (1864).
[6] Werigo: Liebig's Ann., 135, 17 (1865).
[7] Schultz: Ber. chem. Ges. Berlin, 17, 473 (1884).
[8] Am. Jour. Chem., 5, 1 (1883).
[9] Chem. Centralblatt, [5] 7, I, 372 (1903).

iron and caustic soda. Witt[1] dissolved stannous chloride in caustic soda and found that the clear hot solution reduced nitrobenzene to azobenzene. Baeyer[2] showed that nitrosobenzene reacts with aniline in acetic acid solution to form azobenzene according to the empirical equation

$$C_6H_5NO + C_6H_5NH_2 = C_6H_5N : NC_6H_5 + H_2O.$$

This reaction should be studied more in detail as it unquestionably takes place in stages and not as written. Nitrobenzene and alcoholic hydrazobenzene react in three stages.[3]

$$2C_6H_5NO_2 + 3C_6H_5NH.HNC_6H_5 =$$
$$2C_6H_5NO + C_6H_5NH.HNC_6H_5 + 2C_6H_5N : NC_6H_5 + 2H_2O =$$
$$C_6H_5NO + C_6H_5NHOH + 3C_6H_5N : NC_6H_5 + 2H_2O =$$

$$C_6H_5N — NC_6H_5 + 3C_6H_5N : NC_6H_5 + 3H_2O.$$

Anschütz and Schultz[4] obtained azobenzene by the action of sodium on *p*-bromaniline dissolved in anhydrous ether. They are inclined to think that hydrazobenzene was the original product in which case the reaction would be written,

$$2BrC_6H_4NH_2 + 2Na = C_6H_5NH.HNC_6H_5 + 2NaBr.$$

The oxidation of hydrazobenzene to azobenzene takes place very readily and can be carried out by bubbling air through the solution. Unsatisfactory yields of azobenzene can be obtained by oxidizing aniline with permanganate[5] or with bleaching powder.[6] It seems probable that the low yields are due to carelessness in regard to conditions. In view of Baeyer's[7] experiments with nitrosobenzene and aniline in acetic acid solution, it seems as though acetic acid might be a good solvent to start with. It is interesting to

[1] Ber. chem. Ges. Berlin, 18, 2912 (1885).
[2] Ibid., 7, 1639 (1874).
[3] Haber and Schmidt: Zeit. phys. Chem., 32, 280 (1900).
[4] Ber. chem. Ges. Berlin, 9, 1398 (1876).
[5] Glaser: Liebig's Ann., 142, 367 (1867). Hoogewerff and van Dorp: Ber. chem. Ges. Berlin, 10, 1936 (1877); 11, 1202 (1878).
[6] Schmidt: Jour. prakt. Chem., [2] 18, 196 (1878).
[7] Ber. chem. Ges. Berlin, 7, 1639 (1874).

note that Leeds[1] obtained azobenzene by oxidizing aniline in acetic solution with hydrogen peroxide. Weyl[2] has obtained azobenzene by boiling nitrosobenzene with red phosphorus and aqueous alkali. The details will be given under aniline. It is possible that azobenzene is sometimes formed by the dehydration of phenylhydroxylamine.[3]

$$2C_6H_5NHOH = C_6H_5N : NC_6H_5 + 2H_2O.$$

Azobenzene forms orange-red crystals melting at 68°. It boils at 295° and distils unchanged. It is not affected by boiling with acids or alkalies. It is readily reduced to hydrazobenzene. It is not readily oxidized but can be converted into azoxybenzene by chromic acid in acetic acid solution.

Hydrazobenzene

An 80 percent yield of hydrazobenzene can be obtained by treating azobenzene in alcoholic solution with zinc and caustic soda.[4] One can also start from nitrobenzene or from azoxybenzene. The reduction can also be effected by sodium amalgam.[5] Schmidt and Schultz[6] have added hydrogen sulphide to an alcoholic ammonia solution of nitrobenzene. Franzen and Deifel[7] have reduced azobenzene to hydrazobenzene with ethyl magnesium bromide, the reaction taking place in two stages.

$$2C_6H_5N : NC_6H_5 + 2BrMgC_6H_5 = C_4H_{10} + 2C_6H_5N(MgBr).(MgBr)NC_6H_5$$

$$2C_6H_5N(MgBr).(MgBr)NC_6H_5 + 2H_2O = 2C_6H_5NH.HNC_6H_5 + 2MgBrOH.$$

Schischusky[8] has obtained hydrazobenzene by passing aniline vapor over heated lead peroxide.

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[1] Chem. News, 44, 210 (1881).

[2] Ber. chem. Ges. Berlin, 40, 970 (1907).

[3] Cf. Haber: Zeit. phys. Chem., 32, 279 (1900). Löb: Ibid., 34, 664 (1900).

[4] Erdmann: Zeit. angew. Chem., 1893, 1865.

[5] Moltschanowsky: Ber. chem. Ges. Berlin, 15, 1575 (1882).

[6] Liebig's Ann., 207, 329 (1881).

[7] Ber. chem. Ges. Berlin, 38, 2716 (1905).

[8] Ibid., 7, 1456 (1874).

Hydrazobenzene forms colorless crystals melting at 125°. It is easily oxidized to azobenzene; energetic reducing agents convert it into aniline. When distilled, hydrazobenzene breaks down into azobenzene and aniline,

$$2C_6H_5NH.HNC_6H_5 = C_6H_5N : NC_6H_5 + 2C_6H_5NH_2.$$

In acid solutions hydrazobenzene changes rapidly into benzidine (di-*p*-diaminodiphenyl) and to a small extent into diphenylene (*o*-*p*-diaminodiphenyl), semidine (*p*-aminodiphenylamine) being undoubtedly an intermediate product. This reaction takes place so readily that hydrazobenzene is not obtained at all when azobenzene is reduced in acid solutions.

Benzidine

As might be expected from the preceding paragraph, benzidine is usually obtained by the molecular rearrangement of hydrazobenzene in acid solutions, though it is not necessary that the hydrazobenzene should be isolated or should ever be present in appreciable amounts. A 66 percent yield of benzidine is obtained[1] when hydrazobenzene is boiled with hydrochloric acid. Zinin[2] prepared benzidine direct by dissolving azobenzene or azoxybenzene in alcohol and reducing with sulphurous acid. Quite recently Bodenstein[3] has patented an improvement on this method. He suspends azobenzene in an aqueous solution of hydrochloric acid or sulphuric acid, and adds iodine, hydriodic acid or potassium iodide. He then treats the solution with sulphurous acid. The hydriodic acid is the reducing agent. There being no organic solvent, there is no loss of iodine on that account. It is also claimed that less diphenylene is formed under these conditions. Schmidt and Schultz[4] prepared benzidine by treating azobenzene with alcoholic stannous chloride and hydrochloric acid. Benzidine can also be made by the re-

[1] Bender and Erdmann: Chem. Prep., 2, 452 (1894).
[2] Liebig's Ann., 85, 328 (1853).
[3] Chem. Centralblatt, 10, II, 479 (1906).
[4] Liebig's Ann., 207, 330 (1881).

duction of dinitrodiphenyl; but that reduction does not concern us.

Benzidine forms colorless crystals melting at 122°. By oxidation with manganese dioxide and acid it is converted into quinone. The sulphate is very sparingly soluble in water.

Aniline

Aniline is made commercially by reducing nitrobenzene with iron and hydrochloric acid. The hydrochloric acid or rather the ferrous chloride acts as a catalytic agent. When the reaction takes place on a technical scale, the iron is oxidized to ferro-ferric oxide.

$$4C_6H_5NO_2 + 4H_2O + 9Fe = C_6H_5NH_2 + 3Fe_3O_4.$$

When carried out on a small scale the reaction is apt to be more complete, hydrated ferric oxide being formed,

$$C_6H_5NO_2 + H_2O + 2Fe = C_6H_5NH_2 + Fe_2O_3 \text{ (hydrated)}.$$

Acetic acid may be substituted for hydrochloric acid.[1] The yield of aniline is about 90 percent. In the laboratory it is more convenient to make it with tin and hydrochloric acid[2] or with stannous chloride and hydrochloric acid.

Both tin and copper can apparently be used commercially in some cases provided the metals are recovered electrolytically.[3]

If nitrobenzene in alcoholic ammonia solution is heated for a long time at 100° with hydrogen sulphide, a reduction to aniline takes place.[4] An 86 percent yield was obtained[5] by boiling nitrobenzene with zinc and water,

$$C_6H_5NO_2 + H_2O + 3Zn = C_6H_5NH_2 + 3ZnO.$$

Heating with zinc and hydrochloric acid is apt to give chloraniline.[6] Wöhler[7] obtained an unspecified yield by boiling

[1] Bechamp: Ann. Chim. Phys., [3] 42, 186 (1854).
[2] Roussin: Comptes rendus, 52, 797 (1861).
[3] Cf. Zeit. Elektrochemie, 8, 217 (1902).
[4] Zinin: Liebig's Ann., 44, 286 (1842).
[5] Kremer: Jour. prakt. Chem., 90, 255 (1863).
[6] Kork: Ber. chem. Ges. Berlin, 19, 1567 (1886).
[7] Liebig's Ann., 102, 127 (1857).

nitrobenzene with an alkaline sodium arsenite solution. Weyl[1] has reduced nitrobenzene to aniline by heating with red phosphorus and water or alkali. The actual reducing agent is phosphine which appears to be formed from red phosphorus and alkali according to the equation,

$$2P + 3NaOH = Na_3PO_3 + PH_3.$$

With water the reaction is said to be

$$4P + 6H_2O = 3H_3PO_2 + PH_3.$$

If red phosphorus, water and nitrobenzene are heated to 100° in a closed flask, aniline is formed according to the equation,

$$3C_6H_5NO_2 + 4PH_3 = 3C_6H_5NH_2 + 2H_3PO_2 + 2P,$$

the phosphorus of course reacting with water to form more phosphine. If the temperature is raised to 115°, ammonia is formed and practically no aniline. If red phosphorus is heated with caustic soda solution until phosphine is given off freely and if nitrobenzene is then added gradually, aniline is practically the sole product. If, however, nitrobenzene, red phosphorus and a caustic soda solution are mixed and then boiled, only a little aniline is formed. There are some phenols formed and apart from these the main product is azobenzene. Some azoxybenzene is formed and there are traces of hydrazobenzene. Weyl writes the equations,

$$2C_6H_5NO_2 + PH_3 = C_6H_5N\overset{O}{\diagdown\diagup}NC_6H_5 + H_3PO_3$$

$$3C_6H_5N\overset{O}{\diagdown\diagup}NC_6H_5 + PH_3 = 3C_6H_5N : NC_6H_5 + H_3PO_3$$

$$3C_6H_5NO_2 + 4PH_3 = 3C_6H_5NH_2 + 2H_3PO_3 + 2P.$$

Since there is no authentic case of the direct reduction of azoxybenzene to azobenzene, it is probable that the second equation is wrong. A little knowledge of electrochemistry would have been extremely helpful at this point.

When red phosphorus, nitrobenzene and a hydrochloric

[1] Ber. chem. Ges. Berlin, 39, 4340 (1906); 40, 970 (1907).

acid solution are heated in a pressure flask to 140–160°, a mixture of aniline and *p*-chloraniline is obtained.[1]

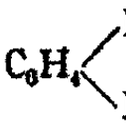
Aniline is a colorless liquid freezing at —8° and boiling at 183°–184°. We have already seen that aniline and nitrosobenzene react in acetic acid solution forming azobenzene.[2] In dilute aqueous sulphuric acid nitrosobenzene reacts with aniline[3] to form phenyl quinone diimide, which polymerizes to emeraldine,

$$2C_6H_5NO + 2C_6H_5NH_2 = C_6H_5N : C_6H_4 : NH + 2C_6H_5NHOH.$$

The phenylhydroxylamine reacts with aniline in dilute aqueous sulphuric acid to form *p*-aminodiphenylamine,

$$C_6H_5NHOH + C_6H_5NH_2 = C_6H_5NHC_6H_4NH_2 + H_2O.$$

When equal volumes of nitrobenzene and aniline are heated with powdered caustic soda,[4] about 30 percent of the aniline is converted into phenazine,

$$C_6H_5NO + C_6H_5NH_2 = C_6H_4\begin{  }C_6H_4 + H_2O.$$

By suitable oxidation of aniline, varying amounts of azobenzene, azoxybenzene, phenylhydroxylamine, nitrosobenzene, nitrobenzene, and *p*-aminophenol can be obtained. When oxidized in acid solution aniline is converted into aniline black, quinone, and quinone derivatives. Aniline reacts with nitrous acid to form diazo compounds,

$$C_6H_5NH_2.HCl + HNO_2 = C_6H_5N_2Cl + 2H_2O.$$

Aniline and formaldehyde condense to $(C_6H_5N : CH_2)_3$.

p-Aminophenol

We have seen that in strongly acid solutions, phenylhydroxylamine changes into *p*-aminophenol

$$C_6H_5NHOH = HOC_6H_4NH_2.$$

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[1] Weyl: Ber. chem. Ges. Berlin, 40, 3609 (1907).
[2] Baeyer: Ber. chem. Ges. Berlin, 7, 1639 (1874).
[3] Nover: Ber. chem. Ges. Berlin, 40, 288 (1907).
[4] Wohl and Aue: Ber. chem. Ges. Berlin, 34, 2442 (1901).

This is one method of making *p*-aminophenol; it can also be made by reduction of *p*-nitrophenol.

Para-aminophenol forms colorless crystals which turn brown readily in the air and which melt with decomposition at about 180°. In alkaline solutions it is a fairly strong reducing agent and the sodium salt is sold as a photographic developer under the name of rodinal.

We can now run over the more interesting electrochemical reductions of nitrobenzene and of its reduction products.

Nitrosobenzene

Dieffenbach[1] has combined the electrolytic reduction of nitrogen to phenylhydroxylamine with the electrolytic oxidation of phenylhydroxylamine to nitrosobenzene. He obtains a good yield (unspecified) by electrolyzing a suspension of nitrobenzene in an aqueous neutral solution of the sulphates of aluminum, magnesium, or the alkalies. No diaphragm is used.

Phenylhydroxylamine

Haber decided that a good yield of phenylhydroxylamine could best be obtained by keeping the solution nearly neutral, so that the phenylhydroxylamine should be as stable as possible. He first used an aqueous acid solution[2] with a platinum tube as cathode. By passing cold water through this tube, the cathode compartment was kept below 20°. The current efficiency is 10–20 percent in absolute amounts of 0.5–0.9 gram phenylhydroxylamine. The acetic acid solution does not conduct well and it was difficult to avoid local heating. Brand[3] therefore suspended nitrobenzene in an aqueous sodium acetate solution to which a little acetic acid was added. The cathode was nickel and the current efficiency seems to have been about 70 percent. Haber[4] has also prepared phenylhydroxylamine by using, as a cathode solution,

[1] Chem. Centralblatt, [5] 2, I, 911 (1908).
[2] Haber: Zeit. Elektrochemie, 4, 513; 5, 77 (1898).
[3] Ber. chem. Ges. Berlin, 38, 3076 (1905).
[4] Zeit. phys. Chem., 32, 272 (1900).

nitrobenzene, ammonium chloride, and ammonia dissolved in aqueous alcohol. When a platinum tube cathode was used, a current efficiency of 38 percent was obtained, about 21 percent of azoxybenzene being formed. The yield was less satisfactory when a lead tube was substituted for the platinum cathode.

Messrs. Boehringer & Sons have adopted a different method.[1] They point out that dissolving in an aqueous solution often requires a large volume of liquid [this would not apply in the case of an emulsion]. They therefore place the nitrobenzene in a porous carbon cup, which serves as a cathode. The nitrobenzene is pressed through the pores of the carbon cup by an excess pressure of half an atmosphere and is reduced at once. The company has really made a nitrobenzene electrode. With a current density of 2 amp/dm^2 and a temperature of less than 25°, nitrobenzene is converted apparently quantitatively to phenylhydroxylamine in spite of the fact that the electrolyte is 30 percent sulphuric acid. A solid organic substance can be treated in the same way by dissolving it in an inert, non-dissociating solvent, the solution then being pressed through the carbon cup.

Azoxybenzene

Haeussermann[2] obtained some azoxybenzene by reducing an alcoholic sulphuric acid solution of nitrobenzene at a platinum cathode. Haber[3] started with a cathode solution consisting of nitrobenzene, caustic soda, alcohol and water. The cathode was platinized platinum and the cathode potential, E_c. was never allowed to become more cathodic than —0.314 volts. The yield of azoxybenzene represented about 76 percent current efficiency. There were also traces of hydrazobenzene and of aniline. A method of this type is only of theoretical interest and it is to Löb[4] that we owe a

[1] Zeit. Elektrochemie, 6, 548 (1900).
[2] Chem. Zeit., 17, 129 (1893).
[3] Zeit. Elektrochemie, 4, 507 (1898).
[4] Ibid., 7, 336; Zeit. phys. Chem., 34, 662 (1900).

practical electrolytic method of preparing azoxybenzene. His method of reasoning was as follows:

"Azoxybenzene is formed by condensation of nitrosobenzene with phenylhydroxylamine, as was proved by Bamberger and by Haber. In presence of free alkali, phenylhydroxylamine changes into azoxybenzene and aniline provided there are no oxidizing agents present. In order to prevent the formation of aniline, the rate of reduction must be kept down to such an extent that the first condensation takes place completely without the concentration of the phenylhydroxylamine increasing sufficiently to make the second reaction take place. This can be done by regulating the current density. If one works with an alkaline, alcoholic solution, however, it appears that some azobenzene is always formed in spite of such precautions as keeping the cathode potential constant and the solution well stirred. This is so, even if the reduction is not carried anywhere near to an end. It seems as though the condensation of two molecules of phenylhydroxylamine to azobenzene always took place to some extent in an alkaline, alcoholic solution or as though the conditions were always favorable for the formation of hydrazobenzene and for its condensation with nitrobenzene to form azobenzene.

"I have found that, when nitrobenzene, is suspended in aqueous caustic soda, electrolytic reduction gives azoxybenzene without azobenzene being formed even when a large excess of electrical energy is run in.

"Bamberger[1] and his pupils have shown that phenylhydroxylamine in aqueous alkaline solution is oxidized by air chiefly to azoxybenzene and nitrobenzene, the former resulting from a condensation of the intermediate oxidation product, nitrosobenzene, with phenylhydroxylamine, while the nitrobenzene is an oxidation product of nitrosobenzene. When there is no air present, phenylhydroxylamine decomposes in aqueous caustic soda, with formation of azoxybenzene and aniline.

[1] Ber. chem. Ges. Berlin, **33**, 271; Liebig's Ann., **311**, 78 (1900).

"In the cathode chamber the action of the oxygen of the air is negligible. Owing to the continuous formation of nitrosobenzene from nitrobenzene and of phenylhydroxylamine from nitrosobenzene, and in consequence of the high rate of condensation of nitrosobenzene with phenylhydroxylamine, azoxybenzene is the sole product. In aqueous caustic soda, phenylhydroxylamine does not condense to azobenzene, as Bamberger found that it did in alcoholic potash, and that is why we get no azobenzene."

Nitrobenzene was suspended in 2–4 percent aqueous caustic soda solution which was stirred vigorously. Either a nickel gauze or a mercury cathode can be used. With a current density of 5–7 amp/dm², a 90 percent current yield of azoxybenzene was obtained. The temperature must be kept below 90° as azobenzene is formed when the reduction takes place at higher temperature. If cathodes of tin, lead or zinc are used, azobenzene is formed, while aniline is the chief product at a spongy copper cathode.[1] The effect of stirring is shown in some of Löb's experiments with a mercury cathode.[2] On short runs, the current efficiency was about 49 percent when there was no stirring and practically 100 percent when the cathode solution was stirred vigorously. By using a large cathode and a small anode, Meister Lucius & Brüning[3] claim to get a satisfactory yield of azoxybenzene by reducing nitrobenzene in aqueous alkaline solution without a diaphragm.

Azobenzene

Elbs and Kopp[4] dissolved nitrobenzene in aqueous alcohol and added sodium acetate to make the solution conduct and to keep it slightly alkaline. They used a nickel gauze cathode and a current of 10 amp/dm². They started with a hot solution which was kept boiling by the current. A 95 percent

[1] Löb: Zeit. Elektrochemie, 9, 753 (1903).
[2] Löb: Zeit. phys. Chem., 34, 655 (1900).
[3] Zeit. Elektrochemie, 8, 217 (1902).
[4] Ibid., 5, 108 (1898).

yield of azobenzene was obtained. Löb[1] substituted a mercury cathode for the nickel gauze one. As was stated under azoxybenzene, Löb[2] obtained azobenzene when electrolyzing an emulsion of nitrobenzene in aqueous alkali at 100° using a mercury or nickel cathode and below 90° when using a cathode of zinc, tin or lead. Bayer and Co.[3] get the same result below 90° with a nickel or lead cathode by adding basic salts of zinc, tin, or lead to the solution. Meister Lucius & Brüning[4] make azobenzene without a diaphragm just as they make azoxybenzene[5] except that the temperature is kept at 105°–115° during the run.

Hydrazobenzene

Hydrazobenzene is prepared electrolytically in the same way as azobenzene[6] except that it is wise to cut down the current density after the azo stage has been reached. Darmstädter[7] adds benzene to the mixture of nitrobenzene and aqueous caustic and electrolyzes with a current density of 2–4 amp/dm², using an iron or nickel cathode and stirring the cathode solution vigorously. The only advantage of this is that it prevents the precipitation of any solid matter on the cathode, azoxybenzene and hydrazobenzene being readily soluble in benzene. To judge from the patent no azobenzene is formed, the reduction being to azoxybenzene and then to hydrazobenzene.

Benzidine

Benzidine can be made without having to isolate hydrazobenzene, by reducing azobenzene or azoxybenzene in acid solution. Under some conditions it can also be made directly from nitrobenzene, though not so satisfactorily. Haeusser-

[1] Zeit. phys. Chem., 34, 661 (1900).
[2] Zeit. Elektrochemie, 9, 753 (1903).
[3] Ibid., 7, 859 (1901).
[4] Ibid., 10, 389 (1904).
[5] Ibid., 8, 217 (1902).
[6] Elbs and Kopp: Zeit. Elektrochemie, 5, 109 (1898). Bayer and Co.: Ibid., 7, 859 (1901).
[7] Zeit. Elektrochemie, 13, 638 (1907).

mann[1] obtained benzidine as the chief product when he electrolyzed nitrobenzene in an alcoholic sulphuric acid solution. Löb[2] had the same experience with alcoholic hydrochloric acid as solvent. Löb[3] also dissolved nitrobenzene in formic acid to which a few cubic centimeters of concentrated sulphuric acid had been added; in glacial acetic acid plus a little sulphuric acid; and in a mixture of acetic acid, oxalic acid and a little sulphuric acid. The temperature was kept at 30°–40° and a platinum cathode was used. In all three cases a current yield of 70–80 percent of benzidine was obtained. The benzidine prepared in this way is not very pure and Löb[4] therefore worked out two better methods. He dissolved azobenzene in alcoholic sulphuric acid and reduced at 30°–35°, using a mercury cathode and very vigorous stirring. His current efficiency was 76–80 percent and the benzidine was pure. In the other method he started with azoxybenzene instead of azobenzene. The temperature was kept down to 25°–30°, and a current efficiency of 80–82 percent was obtained. Löb[5] also succeeded in obtaining a fair yield of benzidine by dissolving azoxybenzene in 25 percent hydrochloric acid, adding a little stannous chloride and electrolyzing at about 80°.

Aniline

Haeussermann[6] and Elbs[7] found that practically no aniline was formed when nitrobenzene was reduced at a platinum cathode in alcoholic sulphuric acid. Aniline is obtained if a zinc or lead cathode be used,[8] though the yield is not very satisfactory. In 1899 the firm of Boehringer & Sons[9] took out a patent for the electrolytic reduction of nitrobenzene to

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[1] Chem.-Ztg., 17, 129 (1893).
[2] Ber. chem. Ges. Berlin, 29, 1894 (1896).
[3] Zeit. Elektrochemie, 4, 471 (1897).
[4] Zeit. phys. Chem., 34, 661 (1900).
[5] Cf. Brand: Ahrensche Sammlung chemischer Vorträge, 13, 125 (1908).
[6] Chem.-Ztg., 17, 129 (1893).
[7] Ibid., 17, 209 (1893).
[8] Elbs: Chem.-Ztg., 17, 209 (1893).
[9] Zeit. Elektrochemie, 7, 570 (1901).

aniline in aqueous or aqueous-alcoholic hydrochloric acid, using a tin cathode. It was also possible to use a nickel cathode provided stannous chloride was added to the solution. It was permissible to use current densities as high as 18 amp/dm², though in this case it was necessary to cool the cathode chamber. The yield is said to be practically quantitative; but it is not clear whether this refers to current yield or to the chemical yield of aniline from a given amount of nitrobenzene. In another patent the firm claims the same results when salts of copper, lead, iron, chromium or mercury are added to the cathode chamber instead of a salt of tin. Instead of the salts of these metals, the metals themselves may be added in a pulverulent form (mercury of course in drops).

The appearance of these patents caused Elbs and Silbermann[1] to publish an account of some work on which they had been engaged since 1899. They found that addition of zinc chloride to the cathode solution caused the formation of aniline. In one case the cathode solution consisted of 75 grams nitrobenzene, 25 grams zinc chloride, 80 cc concentrated HCl, 120 cc alcohol, and 35 cc water. A copper gauze cathode was used and the current yield of aniline was 66–75 percent. The anode was a zinc plate and the anode solution dilute zinc chloride. It seems as though it would have been simpler to have put the zinc anode in the cathode solution and to have done away with a diaphragm entirely.

Under Foerster's direction Chilesotti[2] has repeated and amplified the experiments described in the Boehringer patents. He obtained a current yield of 84 percent of aniline when reducing nitrobenzene and hydrochloric acid in aqueous alcohol. With *m*-nitroaniline a 96 percent yield of *m*-phenylenediamine was obtained. When copper salts were substituted for stannous chloride the yield fell off somewhat.

In later patents Boehringer & Sons[3] prepared aniline or substituted anilines by electrolytic reduction of azobenzene

[1] Zeit. Elektrochemie, 7, 589 (1901).
[2] Ibid., 7, 768 (1901).
[3] Ibid., 8, 216 (1902).

or of substituted azobenzenes. The firm points out that the chemical reduction of nitro and azo compounds to amines by means of tin or copper in acid solutions becomes commercially practicable provided the tin or copper is regenerated electrolytically.[1] Boehringer & Sons[2] have also patented the reduction of nitro-compounds to amines in neutral or alkaline solutions, using a copper cathode and adding copper powder if necessary. Elbs and Brand[3] claim that the wording of this patent does not do full justice to the earlier work of Elbs. They also state that the addition of copper powder is absolutely necessary if *m*-nitroaniline is to be reduced to phenylenediamine.

The firm of Meister Lucius & Brüning[4] patents the reduction of nitro-compounds to amines in acid solution in presence of titanium salts at a lead cathode. It is stated that a diaphragm may sometimes be dispensed with; but there is nothing to show under what conditions this is permissible.

p-Aminophenol

Gattermann[5] tried to obtain aniline by electrolytic reduction at a platinum cathode of nitrobenzene dissolved in concentrated aqueous sulphuric acid; but obtained chiefly *p*-aminophenol instead, due to the change of phenylhydroxylamine. Noyes and Clement[6] used a still more concentrated sulphuric acid (sp. gr. 1.84) and obtained *p*-aminophenol sulphonic acid. In both sets of experiments the temperature was high. Elbs[7] dissolved nitrobenzene in varying mixtures of acetic acid and sulphuric acid. Both aniline and *p*-aminophenol were obtained. With a platinum cathode the aminophenol predominated, while more aniline was formed at a lead cathode. Elbs is inclined to think that the reaction may,

[1] Boehringer and Sons: Zeit. Elektrochemie, 8, 217 (1902).
[2] Zeit. Elektrochemie, 9, 480 (1903).
[3] Ibid., 8, 788 (1902).
[4] Ibid., 12, 688 (1906).
[5] Ber. chem. Ges. Berlin, 26, 1884, 2810 (1893).
[6] Ibid., 26, 990 (1893).
[7] Zeit. Elektrochemie, 2, 472 (1896).

to a certain extent, go through the azoxy stage, the azoxybenzene being converted by the sulphuric acid into *p*-oxyazobenzene[1] which then reduces to a mixture of aniline and *p*-aminophenol,

$$C_6H_5N : NC_6H_4OH + 4H = C_6H_5NH_2 + N_2NC_6H_4OH.$$

Brand[2] states that this assumption has been disproved because Elbs got no appreciable amount of *p*-aminophenol when he started with azoxybenzene, but he gives no reference.

Löb[3] dissolved nitrobenzene in fuming hydrochloric acid. On electrolyzing this solution he obtained a mixture of *o*- and *p*-chloraniline. There is undoubtedly an intermediate formation of phenylchloramine which then changes into chloraniline,

$$C_6H_5NHCl = ClC_6H_5NH_2.$$

Darmstädter[4] has improved the Gattermann process by using an emulsion of nitrobenzene in a more dilute sulphuric acid (50 percent), and by stirring vigorously. In this way he keeps down the yield of aniline. He also finds that 80 percent of the nitrobenzene can be converted into *p*-aminophenol at a carbon cathode, 40 percent at a copper cathode and only 30 percent at a tin cathode. Brand[5] recommends the use of silver cathodes. The difference between Darmstädter's process for making *p*-aminophenol and that of Boehringer & Sons for making phenylhydroxylamine seems to be that the acid is more dilute and the temperature is lower when phenylhydroxylamine is to be made.

Emeraldine

Reference has previously been made to the fact that, in dilute aqueous sulphuric acid solutions, nitrosobenzene reacts

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[1] Wallace: Ber. chem. Ges. Berlin, 13, 525 (1880); 14, 2617 (1881).
[2] Ahrensche Sammlung chemischer Vorträge, 13, 140 (1908).
[3] Ber. chem. Ges. Berlin, 29, 1894 (1896).
[4] Zeit. Elektrochemie, 11, 274 (1905).
[5] Ahrensche Sammlung chemischer Vorträge, 13, 142 (1908).

with aniline[1] to form phenyl quinone diimide, which polymerizes to emeraldine,

$$2C_6H_5NO + 2C_6H_5NH_2 = C_6H_5N{:}C_6H_4{:}NH + 2C_6H_5NHOH.$$

This same reaction is carried out electrolytically by dissolving nitrobenzene either in 50 percent $NaHSO_4$ or in H_2SiF_6 (sp. gr. 1.3) and reducing at a nickel gauze cathode with a current density of about 1.3 amp/dm^2.

In Table I is given a summary of the facts outlined in the preceding pages, the chemical and the electrolytic methods being given in parallel columns. When the two coincide they are placed abreast, and a blank space in one column means that there is no method corresponding to the one in the other column.

TABLE I

Chemical methods	Electrolytic methods
Nitrosobenzene	
Direct or indirect oxidation of phenylhydroxylamine	Reduction of nitrobenzene to phenylhydroxylamine and oxidation of the phenylhydroxylamine
Nitrosyl bromide and mercury diphenyl	
Nitrosyl chloride and phenyl magnesium bromide	
Phenylhydroxylamine	
Nitrobenzene, aqueous $CaCl_2$ or NH_4Cl and zinc, zinc dust or zinc amalgam	
Oxidation of aniline	
	Nitrobenzene, alcoholic $NH_4Cl + NH_3$; platinum cathode
	Nitrobenzene, aqueous acetic acid plus sodium acetate; nickel cathode
	Nitrobenzene, 30 percent H_2SO_4, porous carbon cathode

[1] Nover: Ber. chem. Ges. Berlin, 40, 288 (1907).

TABLE I—(*Continued*)

Chemical methods	Electrolytic methods
Azoxybenzene	
Nitrobenzene, sodium methylate, methyl alcohol	
Nitrobenzene, caustic soda and methyl alcohol	Nitrobenzene, aqueous alcoholic NaOH; platinized cathode and definite cathode potential
Nitrobenzene, sodium amalgam and alcohol	Nitrobenzene, aqueous NaOH; mercury or nickel cathode
Nitrobenzene, zinc dust, aqueous NaOH or NH_4OH	
Nitrobenzene, zinc dust, aqueous $CaCl_2$ or NaCl at 105°–110°	
Nitrobenzene, aqueous sodium, arsenite, boiling	
Nitrobenzene, iron and aqueous NaOH, hot	
Nitrosobenzene and phenyl hydroxylamine	
Nitrobenzene and dry caustic potash	
Nitrosobenzene, KOH and CH_3OH	
Oxidation of aniline or azobenzene	
Azobenzene	
Distillation of azoxybenzene	
Azoxybenzene and iron filings	
Nitrobenzene, sodium amalgam, alcohol, acetic acid	Nitrobenzene, alcoholic sodium acetate; mercury or nickel cathode
Nitrobenzene, sodium amalgam, wet ether	Nitrobenzene, aqueous NaOH, mercury, or nickel cathode
Nitrobenzene, zinc and alcoholic NaOH or NH_4OH	Nitrobenzene, aqueous caustic soda; zinc, tin or lead cathode below 90°
Nitrobenzene, aqueous sodium stannite	Nitrobenzene, aqueous NaOH, salts of tin, lead or zinc; nickel or lead cathode

TABLE I—(*Continued*)

Chemical methods	Electrolytic methods
Nitrobenzene, or azobenzene, iron and aqueous caustic soda	
Nitrosobenzene, aniline, acetic acid	
Nitrobenzene, alcoholic hydrazobenzene	
Nitrobenzene, red phosphorus, aqueous NaOH	
Bromaniline, sodium, ether (air)	
Oxidation of hydrazobenzene	
Oxidation of aniline	
Hydrazobenzene	
Nitrobenzene, azoxybenzene or azobenzene, water and sodium amalgam	Nitrobenzene or azobenzene, alcoholic sodium acetate; mercury or nickel cathode
Nitrobenzene, azoxybenzene or azobenzene, zinc and aqueous NaOH	Nitrobenzene, aqueous NaOH; iron or nickel cathode
Nitrobenzene, alcoholic ammonia, H_2S	
Azobenzene, ethyl magnesium bromide, water	
Aniline vapor and heated PbO_2	
Benzidine	
Hydrazobenzene and acid	Azobenzene or azoxybenzene, alcoholic H_2SO_4; mercury cathode
Azobenzene, or azoxybenzene, alcohol, sulphurous acid	
Azobenzene, aqueous HCl or H_2SO_4, I_2 or KI, sulphurous acid	
Azobenzene, alcoholic stannous chloride, hydrochloric acid	

TABLE I—(*Continued*)

Chemical methods	Electrolytic methods
	Aniline
Nitrobenzene, iron or tin, hydrochloric or acetic acid	Nitrobenzene, hydrochloric acid, iron or tin cathode
Nitrobenzene, copper acid	Nitrobenzene, HCl; copper cathode
Nitrobenzene, zinc and water	Nitrobenzene, aqueous alcoholic H_2SO_4; zinc cathode
Nitrobenzene, stannous chloride, HCl	
Nitrobenzene, alcoholic ammonia, H_2S	
Nitrobenzene, alkaline sodium arsenite	
Nitrobenzene, red phosphorus, water or aqueous NaOH	
	Nitrobenzene, neutral or alkaline solutions; copper cathode, copper powder
Azobenzene, tin or copper, in acid solutions	Azobenzene, salts of copper, lead iron, tin, mercury, chromium, titanium in acid solutions; nickel cathode
	p-Aminophenol
Phenylhydroxylamine, conc. H_2SO_4	Nitrobenzene, conc. H_2SO_4; platinum cathode
	Nitrobenzene, acetic and sulphuric acids; platinum cathode
	Nitrobenzene, 50 percent H_2SO_4; carbon cathode
Reduction of *p*-nitrophenol	
	Emeraldine
Aniline and nitrosobenzene in aqueous sulphuric acid	Nitrobenzene, 50 percent $NaHSO_4$ or H_2SiF_6 (sp. gr. 1.3); nickel cathode

According to the results as tabulated, there are forty-nine chemical and twenty-two electrolytic methods of preparing the nine substances. About fifteen of the chemical

methods have been duplicated electrochemically, the others not being paralleled. The exact number is not of any importance because slight shifts could easily be made in the table. Thus Haber's preparation of phenylhydroxylamine in an alcoholic, ammoniacal, ammonium chloride solution, using a platinum cathode might be considered equivalent to the reduction of nitrobenzene in an ammonium chloride solution with zinc dust. I have separated the two because Haber obtained such a poor current efficiency. It is consequently probable that better results would be obtained with a zinc cathode. Under the heading of azoxybenzene the reaction between nitrosobenzene and phenylhydroxylamine takes place in all the electrochemical reductions, though the intermediate compounds are *not* isolated. The chemical preparation of *p*-aminophenol from *p*-nitrophenol could of course be duplicated electrolytically by starting from nitrophenol and doing an aniline reduction. On the other hand, it would have been possible to have made special electrolytic methods out of the preparation of azobenzene with chromium or titanium salts in acid solutions using a nickel cathode. Taking it all in all, Table I gives a fairly accurate presentation of the facts and brings out clearly that a great deal more comparative work remains to be done, before we can be certain that we have worked out the best methods possible.

There is one defect common to nearly all the electrolytic methods given in Table I. A porous cup is necessary for the purpose of preventing oxidation at the anode. This is expensive as regards energy consumption because the resistance is greater, due to the increased distance between the electrodes and to the resistance of the porous cup itself. There is also an increase of voltage owing to polarization at the insoluble anode. The porous cups themselves are a source of trouble and expense. The successful use of soluble anodes would eliminate such objectionable factors as anode polarization and oxidation, while it would decrease greatly the energy loss due to internal resistance.

The experiments to be described in this paper were

undertaken in order to work out an electrolytic method of reducing nitrobenzene to aniline without making use of a porous cup or a platinum anode.

In the commercial reduction of nitrobenzene to aniline, finely-divided metallic iron is allowed to react with nitrobenzene in presence of ferrous chloride at a temperature of about 100°. The amount of ferrous chloride is immaterial as the salt apparently acts as a catalytic agent, the main reaction being the formation of aniline and ferro-ferric oxide according to the equation,

$$4C_6H_5NO_2 + 9Fe + 4H_2O = 4C_6H_5NH_2 + 3Fe_3O_4.$$

An electrolytic cell to duplicate the chemical reaction would consist of iron electrodes in a solution of ferrous chloride at 100° or above, with nitrobenzene in suspension in the solution. The current corrodes iron to ferrous chloride at the anode while an equivalent quantity of iron tends to precipitate at the cathode. Instead of a precipitation of iron we get a reduction of nitrobenzene to aniline and an oxidation of the iron salt to ferro-ferric oxide which precipitates and is thereby removed from the sphere of reaction.

It may be asked why there is any need of an electric current. Why not allow the nitrobenzene to react with the electrode and thus avoid the expenditure of electrical energy? The following experiments appear to answer this question. If 50 grams nitrobenzene and 250 cc of a gram-molecular solution of ferrous chloride, containing considerable free hydrochloric acid are boiled for eight or ten hours in contact with pieces of sheet iron in a round-bottomed flask fitted with a return condenser, no action takes place except that the iron and the hydrochloric acid form ferrous chloride and hydrogen. There is no appreciable reduction of nitrobenzene to aniline.

In a second experiment the iron was omitted and then the only reaction seemed to be a slight oxidation of ferrous chloride to ferric chloride, probably caused by the oxygen of the air.

In a third experiment the massive iron of the first ex-

periment was replaced by iron powder, most of which would pass a 40-mesh sieve. In this case aniline and ferro-ferric oxide were formed when the solution was boiled.

These experiments seemed to prove that neither ferrous chloride nor massive iron in presence of ferrous chloride would reduce nitrobenzene chemically; but that finely divided iron would do so. As this coincided with technical practice, there seemed at the time no reason to doubt the accuracy of the conclusions.

An electrolytic cell was therefore made from a wide glass tube, one end of which was closed by melting the glass together, thus making the equivalent of a large, strong beaker, 5.5 cm in diameter and 17 cm high. This was fitted with a cork through which wires from the electrode passed, the cork also keeping the electrodes in position along the sides of the cell. Through the cork was passed a rapidly rotating stirrer of iron wire. This was revolved at a speed of 1500–2000 r. p. m. by means of a small motor directly connected. The cell was sunk almost to the top in a water bath kept at 100°. The only opening in the cell was the hole through which the stirrer passed loosely. Since the opening was small and since the electrolyte could not boil at 100° on account of the dissolved ferrous chloride, it was assumed that but little nitrobenzene or aniline would be lost by evaporation. The amount of electrolyte used in the cell was 175 cc and the immersed surface of each electrode was 80 cm^2, counting both sides of the electrode.

The solution contained 30 grams nitrobenzene and 10.6 grams iron as neutral ferrous chloride. In the first run, it was electrolyzed for five hours with a current of half an ampere. If we consider only one side of each electrode as effective, the cathode and the anode surfaces are 40 cm^2 each and the current density is 1.25 amp/dm^2. In all the runs made with this apparatus, this is the basis for expressing the current density.

At the end of the runs the solution was still neutral, containing practically the same amount of ferrous iron as was

originally added, and contained only a trace of ferric iron. The solution was filled, however, with red hydrated Fe_2O_3 and the electrodes were covered with a scaling deposit of the same material. Since the amount of ferrous iron in solution at the end of a run did not in any case vary markedly from the amount introduced at the beginning, it was assumed that the iron lost by both electrodes had been oxidized either by the nitrobenzene or by what air may have been present.

In order to analyze for the aniline formed during a run, the potassium bromate method was used. This method depends on the formation of tribromaniline in sulphuric acid solution by the reaction between $KBrO_3$ and KBr which gives free bromine. The aniline takes up the bromine immediately and when the analyst observes the free bromine liberated from the excess of KBr, the addition of the standard $KBrO_3$ solution is stopped and a few crystals of KI are added. The free iodine, corresponding to the excess of bromine, is titrated back with sodium thiosulphate, using starch iodide as indicator. This method is not affected by traces of azobenzene, azoxybenzene or nitrobenzene.

The acidified electrolyte was diluted with three to four volumes of water and distilled until all the nitrobenzene had distilled off with the steam. The unchanged nitrobenzene was drawn off in a separatory funnel and weighed. The liquid, remaining in the flask after the first distillation, was made alkaline with caustic soda and distilled again until a test with calcium hypochlorite solution showed that no more aniline was coming over. The total aniline distillate was diluted to definite volume (1–2 liters). To aliquot parts were added 25 cc 12 *N* H_2SO_4 and a few crystals of KBr, and the titration carried out with the potassium bromate solution.

A number of runs were made which show the effect of current density. They were made at different times and to clear up different points; but they are all presented together in Table II.

TABLE II

10.6 grams iron as $FeCl_2$ in 175 cc solution. Temperature 100°.

Number of run	1[1]	2	3	4
Nitrobenzene	30.0 g.	35.0 g.	30.0 g.	30.0 g.
Cathode loss	0.2 g.	1.0 g.	0.4 g.	4.5 g.
Anode loss	9.5 g.	6.1 g.	14.2 g.	11.6 g.
Aniline formed	5.7 g.	5.6 g.	11.2 g.	10.4 g.
Nitrobenzene recovered		24.5 g.	10.3 g.	10.3 g.
Iron efficiency	71%	95%	92%	78%
Volts	2.2	1.3	0.9	0.7
Amp/dm²	15.0	10.0	5.0	3.75
Current efficiency	117%	212%	363%	291%
Time of run	1.0 hr.	1.5 hr.	2.75 hr.	4.0 hr.

Number of run	5	6	7	8
Nitrobenzene	30.0 g.	34.2 g.	30.0 g.	30.0 g.
Cathode loss	6.3 g.	3.7 g.	13.6 g.	12.7 g.
Anode loss	15.3 g.	18.8 g.	16.0 g.	13.2 g.
Aniline formed	14.8 g.	13.2 g.	17.6 g.	16.8 g.
Nitrobenzene recovered	3.1 g.	4.2 g.	1.0 g.	1.0 g.
Iron efficiency	83%	71%	72%	78%
Volts	0.5	0.45	0.06	0.0
Amp/dm²	2.5	1.25	0.35	0.0
Current efficiency	592%	1000%	3289%	∞
Time of run	5.1 hr.	5.0 hr.	6.5 hr.	6.5 hr.

When considering iron efficiency, 112 grams of metallic iron are taken as being capable of reducing 123 grams of nitrobenzene to 93 grams of aniline. Therefore 1 gram of iron is theoretically equivalent to 0.83 gram of aniline. The iron efficiency is the percentage ratio of the actual amount of aniline formed to the amount of aniline theoretically equivalent to the actual loss in metallic iron.

With the exception of the run at 3.75 amp/dm², where some aniline seems to have been lost, the runs show increasing current efficiency with decreasing current density. Disregarding for the moment the last two runs, which were done

[1] Some pulverulent iron deposited on cathode in this run. All solutions contain hydrated ferric oxide at end of run.

later and which solve the mystery, it will be noted that the apparent current efficiencies lie between 100 percent and 1000 percent.

There are several possible ways of accounting for apparent efficiencies above 100 percent. The electrodes change from metallic iron to ferric iron and we therefore have three valences available for each atomic weight. It is not necessary, however, that this whole change should be effected by the current. In the electrolytic reduction, nitrobenzene is changed at the cathode into nitrosobenzene, a change calling for two equivalents. Therefore three molecular weights of nitrobenzene would be reduced to nitrosobenzene for every two atomic weights of metallic iron corroding electrolytically at the anode to ferrous iron and oxidizing chemically to ferric iron. On this basis the production of nitrosobenzene from nitrobenzene would show an apparent current efficiency of 150 percent. Since nitrosobenzene is more instable than nitrobenzene, it might attack the electrodes directly and be reduced to aniline. In that case the three molecular weights of nitrosobenzene would be reduced chemically to aniline without further consumption of electrical energy. This would mean an increased apparent current efficiency of 300 percent and a total apparent current efficiency of 450 percent. It is not necessary to discuss the probability of this hypothesis because even if true, it would not account for the apparent current efficiencies of 592 percent and 1000 percent obtained in runs 5 and 6. To be on the safe side, however, we made run 7 at the very low current density of 0.35 amp/dm^2. The apparent current efficiency of about 3300 percent is absolutely fatal to any hypothesis which postulates any definite relation between the amount of current and the amount of aniline. This run made it certain that there was a direct chemical reduction of nitrobenzene by iron which was superposed on the electrolytic reduction. Run 8 showed that the current was absolutely unnecessary for the reduction. The same cell was used as in the previous runs but the terminals were not connected to the source of current at all. It should be

noted that the amount of iron dissolved from the cathode approaches more closely to the anode loss as the current density decreases, except in the case of run 6 where some other factor must have come in. It is not to be expected that the two losses would ever be exactly equal because the relative values would change with differences as in the stirring.

It now becomes a question why no reduction to aniline was obtained in the preliminary chemical experiment, since run 8 shows that massive iron will reduce nitrobenzene. The difference between the two experiments seems to be a question of stirring. In the first experiment the mixture of nitrobenzene, massive iron, and ferrous chloride solution was stirred by boiling, while in run 8 a stirrer was used which agitated the solution sufficiently to produce an emulsion. From these experiments it seems probable that massive iron could be used in the technical production of aniline provided the nitrobenzene were brought into intimate contact with the metal by stirring or by other means.

From Table II it appears that the iron efficiencies are low in a number of cases. The most probable explanations for this are that some aniline may be adsorbed by the ferric oxide or that other reduction products are formed. Some oxidation by air undoubtedly takes place. If metallic iron could corrode in some way to univalent iron without doing any reduction, and if the change from the hypothetical, univalent iron to ferric iron did the reducing, we should only have two equivalents available instead of three. What would be 100 percent on this assumption would be only 66 percent efficiency when calculated as in Table II. While it was very improbable, that anything of this sort occurred, it seemed desirable to test whether univalent iron was a possibility.

A solution of ferrous chloride, 300 cc water, and 172 grams $FeCl_2$, was heated above 85° in an open beaker and was stirred vigorously with a glass stirrer. A strip of iron such as was used for electrodes in the electrolytic work, was placed in the solution, as was also a test tube through which cold

water could be passed. These conditions were expected to be suitable for the formation of sub-ferrous chloride which would be carried by the rapid stirring to the cold tube after having been formed at the surface of the iron. At lower temperatures the hypothetical sub-chloride would be instable and would hydrolyze to ferrous chloride and ferrous hydroxide, which latter would be oxidized by the air and would form a yellow precipitate on the surface of the cold tube. After a run of six and one-half hours the iron was found to have lost 1.9 grams in weight and the solution contained a certain amount of suspended, red, hydrated ferric oxide. A second run without the cold tube showed an iron loss of 1.2 grams. In order to show that the air had an effect in the first run, another run was made under the same conditions except that the cell was nearly closed and was kept filled with coal gas which would not tend to oxidize the iron in solution. This run showed an iron loss of only 0.3 gram in seven hours. The solution contained a small amount of very finely divided black precipitate. Since the air is evidently the chief corroding agent in the experiment with the cold tube, the formation of univalent iron has yet to be established. In any case it is a negligible factor so far as the reduction of nitrobenzene is concerned.

A series of runs were next made to clear up various points. The runs were made at 100°, without current; and the solution was stirred by means of a glass stirrer except when otherwise specified. Hydrated ferric oxide was the insoluble compound formed in every case except in run 3. The cell used was the one in which the runs of Table II were made. The results are given in Table III. Run 1 was made for the purpose of studying the effect of stirring. The solution in this run was kept quiet and only a small amount of aniline was formed. In run 2 the iron salt was omitted, the solution consisting of nitrobenzene and water only. Only a very slight reduction takes place and the iron loss is small. Owing to the small amount of corrosion, the ratio between iron and aniline has no significance. This run shows that the ferrous

TABLE III

30.0 gram nitrobenzene and 175 cc solution. Temperature 100°.

Number of run	1[1]	2	3[2]	4[3]	5
Iron in solution	10.6 g.	0.0 g.	24.3 g.	0.0 g.	Ferric acetate
Salt	$FeCl_2$		$FeCl_2$	NaCl	Ferric acetate
Iron loss	2.3 g.	1.0 g.	29.0 g.	2.2 g.	29.3 g.
Aniline formed	1.4 g.	1.0 g.	19.2 g.	0.9 g.	16.9 g.
Nitrobenzene recovered	24.9 g.	23.7 g.	0	27.4 g.	2.0 g.
Iron efficiency			80%		70%
Time of run	4.5 hr.	5.5 hr.	6.0 hr.	7.4 hr.	5.3 hr.

Number of run	6	7	8	9
Iron in solution	1.1 g.	1.1 g.	10.6 g.	10.6 g.
Salt	Ferrous benzoate	$FeCl_2$	$FeSO_4$	$FeCl_2$
Aniline formed	0	0.5 g.	4.7 g.	18.5 g.
Nitrobenzene recovered		20.0 g.	15.6 g.	1.0 g.
Iron efficiency			66%	88%
Time of run	7.3 hr.	7.3 hr.	7.0 hr.	6.5 hr.

chloride is an important factor in the reaction even though its concentration does not change. It apparently acts as a catalytic agent. Run 3 shows the effect of increasing the ferrous chloride concentration. With 24.3 grams of ferrous iron in solution, a yield of 19.2 grams of aniline was obtained in a six-hour run while 16.8 grams of aniline was obtained in a six-hour and a half run with 10.6 grams ferrous iron in solution as shown by run 8 in Table II, or 18.5 grams of aniline as shown by run 9 in Table III. More than doubling the concentration of ferrous chloride does not produce a corresponding increase in the amount of aniline formed. In this run the oxide of iron was black and not red. It seems prob-

[1] No stirring used in this run.

[2] In this run the precipitate was black; red in all the other runs.

[3] Perceptible amounts of nitrosobenzene were formed in this run.

able that this is connected in some way with the higher concentration of the ferrous chloride; but the time at my disposal did not permit of my following up this point.

While these experiments show that ferrous chloride acts as a catalytic agent and that its effect is not proportional to the concentration over wide ranges of concentration, there is nothing to show whether ferrous iron or chlorine as ion is the real catalytic agent. Runs 4–9 were made to clear up this point. In run 4 sodium chloride was substituted for ferrous chloride, the chloride concentration being kept practically the same. Less than 1 gram of aniline was formed in a run lasting over seven hours, so that it is clear that chlorine as ion is not the important factor. One interesting thing about this run was that the nitrobenzene distillate was distinctly greenish, apparently owing to the presence of nitrosobenzene. I do not know to what extent it would be possible to increase the concentration of nitrosobenzene in this way; but the matter seems worth following up.

In run 5 37.3 grams of ferric acetate were dissolved in 175 cc of solution. Under these conditions corrosion took place as usual, giving a fair iron efficiency. The solution was almost glue-like with precipitated ferric hydroxide, part of which undoubtedly came from the hydrolysis of the ferric acetate. This experiment rather indicates that the important thing is the amount of iron in solution, regardless whether it is ferric or ferrous iron. On the other hand it is quite possible that there was a high concentration of ferrous iron in the surface film between metallic iron and the ferric acetate solution.

It seemed desirable to try other iron salts and run 6 was made with a solution of ferrous benzoate. Considerable trouble was experienced in preparing ferrous benzoate, since the basic salt persists in forming and precipitating, leaving only a small quantity of iron in the solution. The ferrous benzoate was made by dissolving finely powdered iron in a hot solution of benzoic acid. The iron content of the solution used in the cell was determined by analysis. There was no

appreciable corrosion of the iron and no aniline was formed. This was quite unexpected; but it seemed possible that this was due to the low concentration of iron, 1.1 gram per 175 cc. To test this run 7 was made, in which a ferrous chloride solution was used having the same iron content as the ferrous benzoate solution in run 6. A very low yield of aniline was obtained so that the hypothesis seemed to be justified. Since some aniline was obtained in run 7 and none in run 6, it seemed possible that the nature of the acid radical might have some effect. To test this, run 8 was made with a ferrous sulphate solution containing the customary 10.6 grams of iron in 175 cc of the solution. The reaction takes place more slowly than when using an equivalent solution of ferrous chloride, the iron efficiency, however, comparing favorably with those of other runs. With the sulphate only 4.7 grams of aniline were obtained in a run of seven hours as compared with 16.8 grams (run 8 in Table II) and 18.5 grams (run 9 in Table III) in a run of six and one-half hours with a ferrous chloride solution. It seems clear from this that the amount of iron in solution and the nature of the acid radical are both factors.

Although it had been assumed in the foregoing experiments that practically no aniline and no nitrobenzene would be lost by volatilization from the cell, yet there was a possibility that some might pass out round the stirrer. Consequently, I constructed an improved cell with a perfectly tight stirrer and a return condenser having a very long, coiled condensing tube. Coal gas was passed through the cell, during the run and was kept burning at the outer end of the condenser. Run 9 was made with this piece of apparatus. The high iron efficiency is undoubtedly due to the retention of all aniline vapor and to the fact that no air was present. I had hoped to make a series of runs with this apparatus, duplicating most of the preceding experiments; but external circumstances have made this impossible.

These experiments have shown that massive iron reacts with nitrobenzene at 100° when in contact with an aqueous

ferrous chloride solution. Although the ferrous chloride content of the solution remains unchanged during the reaction, we cannot dispense with the ferrous chloride, except by substituting some other salt of iron. What part does the ferrous chloride play in the reaction? The most plausible assumption would be that metallic iron and ferrous chloride reacted to form small amounts of a sub-chloride, just as metallic copper and cupric sulphate react to form small amounts of cuprous sulphate. We could then postulate that univalent iron, or something like that, was the real reducing agent. Unfortunately, the experiments on the existence of univalent iron were not of a nature to confirm this hypothesis.

Instead of saying that ferrous chloride catalyzes the reaction between iron and nitrobenzene, we can express it differently and can say that the iron is inert or passive when no ferrous chloride is present. From this point of view, the ferrous chloride keeps the iron from becoming passive. Is there any justification for such a statement? Some light is thrown on this matter by the following quotation from Faraday.[1]

"If a piece of ordinary iron wire be plunged wholly or in part into nitric acid of about specific gravity 1.3 or 1.35, and after action was commenced it be touched by a piece of platina wire, also dipping into the acid, the action between the acid and the iron wire is instantly stopped. The immersed portion of the iron becomes quite bright and remains so, and is in fact in the same state, and can be used in the same manner as the iron rendered inactive by the means already described. This protecting power of platina with respect to iron is very constant and distinct, and is the more striking as being an effect the very reverse of that which might have been anticipated prior to the knowledge of M. Schoenbein's results. It is equally exerted if the communication between it and the iron is not immediate, but made by other metals; as, for instance, the wire of a galvanometer; and if the other circum-

[1] Experimental Researches, 2, 240.

stances be favorable, a small surface of platina will reduce and nullify the action of the acid upon a surface of iron.

"This effect is the more striking if it be contrasted with that produced by zinc; for the latter metal instead of protecting the iron, throws it into violent action with the nitric acid, and determines its quick and complete solution. The phenomena are well observed by putting the iron wire into nitric acid of the given strength, and touching it in the acid alternately by pieces of platina and zinc: it becomes active or inactive accordingly; being preserved by association with the platina and corroded by association with the zinc. So also, as M. Schoenbein has stated, if iron be made the negative electrode of a battery containing from two to ten or more plates in such acid, it is violently acted upon; but when rendered the positive electrode, although oxidized and dissolved, the process, comparatively, is slow."

From this account it appears that iron will corrode in nitric acid of certain strength when not in contact with platinum but will not do so when in contact with platinum. In the second case only the anode reduction takes place at the surface of the iron, all reduction taking place at the surface of the platinum. When we have iron alone in the nitric acid, both the anode and the cathode reactions take place at the surface of the iron. The reducing action at the cathode is sufficient experimentally to counteract the tendency of the anode reaction to make the iron passive. A necessary corollary from this is that any reducing agent of sufficient strength would prevent the iron from becoming passive. There are no quantitative data as yet as to the strength of the reducing agent necessary to keep iron from becoming passive under any given circumstances; but it seems probable that ferrous chloride is a sufficiently strong reducing agent to prevent iron from becoming passive in presence of nitrobenzene. This explanation has the advantage of accounting to a certain extent for the behavior of the acid radical in the iron salt. We know that nickel scarcely corrodes at all when made anode in a sodium sulphate solution, while it corrodes quantitatively

when made anode in a sodium chloride solution. In other words a sulphate solution is more effective than a chloride solution in making nickel passive. It works the same way with aluminum. We have also the belief of the electroplaters that iron rusts more readily if plated with nickel from a chloride solution than if plated from a sulphate solution. In view of these facts we should naturally conclude that a ferrous sulphate solution would not keep iron as active as a ferrous chloride solution would. In runs 8 and 9 of Table III we saw that changing from sulphate to chloride increased the yield of aniline from under 5 grams to over 18 grams (nearly 17 grams in run 8 of Table II). The difference between ferrous chloride and ferrous benzoate, if real, is to be accounted for in the same way. The case of ferric acetate will have to be left out of consideration for the present.

A necessary consequence of this explanation is that it should be possible to find other reducing agents which would not in themselves reduce nitrobenzene but which would cause nitrobenzene to react with iron. Unfortunately, this explanation was not suggested until after the experimental work was finished. I have, therefore, not been able to test the matter. The experiment will be tried at some future time in the Cornell laboratory.

The work on the electrolytic reduction of nitrobenzene was supplemented by some experiments on the reduction of nitrobenzene by reducing agents. Since we can get reducing agents of almost any strength, it ought to be possible to obtain any reduction product of nitrobenzene by attacking the problem systematically. My own work along this line has been purely of a preliminary nature; but the matter has been carried further by Mr. H. C. Allen.

The electrochemical potentials of a number of reducing agents have been determined by Bancroft.[1] Of the inorganic reducing agents, it seemed worth while to try sodium arsenite, potassium ferrocyanide, sodium sulphide, and ferrous hy-

[1] Zeit. phys. Chem., 10, 387 (1892).

droxide. From the published potentials potassium ferrocyanide in alkaline solution ought to be a more powerful reducing agent than sodium arsenite. This is not the case, because no perceptible reduction of nitrobenzene was obtained with potassium ferrocyanide. This is probably due to the fact that the potential of a ferrocyanide solution drops very rapidly when small amounts of ferricyanide are formed. It is also possible that an excess of alkali raises the potential of sodium arsenite above that of potassium ferrocyanide. A third possibility is that the apparent discrepancy in the results may be due to the difference in temperature, the electrical measurements having been made at about 17° and my experiments at boiling temperatures. The work of Boehringer & Sons[1] on the electrolytic reduction of nitrates and nitrites has shown that we may have very marked displacements with rise of temperature.

Since the addition of alkali increases the potential of a reducing agent, it was hoped that in some cases it might be possible to get a difference in reaction product depending on the order in which we add the three reagents, nitrobenzene, reducing agent and alkali. We postulate that the reducing agent will not react with nitrobenzene when the solution is neutral and that such reaction products as azobenzene and azoxybenzene are not reduced to aniline. We should expect the differences to be more marked if all the reagents and all the reaction products were readily miscible because it is only under these conditions that we can get wide variations in concentrations. This is not the case with nitrobenzene, but it did not seem advisable to add alcohol until the simpler system had been studied. A wider range of concentrations could have been obtained by using hydroquinone or pyrogallol as the reducing agent instead of ferrous sulphate, for instance; but there was always the possibility of complications due to the organic compounds and their reduction products, so no experiments have been made as yet with these substances.

[1] Zeit. Elektrochemie, 12, 745 (1906).

There are three different ways in which the three reagents can be mixed:

1. The nitrobenzene may be added to the hot mixture of reducing agent and sodium hydroxide. In this case we have the greatest reducing power and a relatively large excess of the reducing agent. Consequently we should expect to get the maximum reduction.

2. The sodium hydroxide solution may be added to the hot mixture of reducing agent and nitrobenzene. In this case we have the weakest reducing power and no excess of reducing agent or of nitrobenzene.

3. The solution of the reducing agent may be added to the heated mixture of nitrobenzene and alkali. Under these circumstances we get great reducing power but an excess of nitrobenzene. We should therefore not expect to have reduction carried so far.

For the experimental work the following conditions were maintained. All solutions were made up so as to reduce 20.5 grams of nitrobenzene to aniline and then less nitrobenzene was always taken so as to ensure that there would be no nitrobenzene left over. The apparatus consisted of a three-liter, round-bottomed flask fitted with a return condenser and heated by a triple burner. The solution in the flask was always heated to boiling and kept boiling rapidly while the rest of the substances were added drop by drop. The reducing agent was made up to 750 cc with water while the alkali was diluted to 250 cc with water, so that the total mixture was always about one liter. One hundred grams (81.5 percent) NaOH were found to be sufficient to make and keep the solution extremely alkaline in every case.

The contents of the flask were kept boiling vigorously for about half an hour after the mixture was complete. The aniline was distilled with steam from the alkaline mixture and was determined by the bromate method. Azobenzene and azoxybenzene were obtained by extraction with ether. These two substances are miscible in all proportions in the ol id and the liquid states, and I could not find in the litera-

ture any satisfactory method for the separation and determination. They are each soluble to about the same extent in the commoner organic solvents and their boiling points, although widely different, are nevertheless so high as to make impracticable any method depending on this property. A method was devised which is fairly satisfactory in case no other substances are present. It was found that any given mixture of the two constituents had a melting point which was constant and sharply defined to within 0.5°, so I determined the melting points of a number of mixtures of known content, prepared by mixing the pure components and melting them together. The melting points of the homogeneous mixtures were determined in small melting point tubes, such as are used by organic chemists, with a thermometer graduated to 0.1°. The heating was done in a melting point apparatus with water as the medium. There is a minimum in the curve since a mixture containing 21.3 percent azobenzene melts at 25°, while azobenzene melts at 66.5° and azoxybenzene at 35.5°. The exact position of the minimum was not determined but it apparently occurs at a composition of 80–90 percent azoxybenzene. A curve was constructed from the data and it was possible then to read off the composition of any unknown mixture so soon as its melting point was determined. Mixtures melting below 35.5° might of course lie on either side of the minimum. In case of doubt the addition of either of the pure components and remelting will give a mixture with a melting point either higher or lower than that of the original mixture. The second determination shows on which part of the curve the actual composition of the original mixture is located.

In Table IV are given the results of some experiments with ferrous sulphate, sodium sulphide, and sodium arsenite.

Ferrous sulphate alone will not reduce nitrobenzene. If the nitrobenzene is added to the mixture of ferrous sulphate and alkali, we should expect the maximum reduction. Under these conditions we get 78 percent of aniline. It was hoped that addition of alkali to the mixture of ferrous sulphate

TABLE IV

15 grams nitrobenzene and 81.5 grams NaOH per liter. Boiling temperature

Reducing agent	Grams per liter	Aniline	Azoxy-benzene	Azobenzene
$FeSO_4.7H_2O$(A)	210	98%		Trace
$FeSO_4.7H_2O$(B)	210	77%		
$FeSO_4.7H_2O$(C)	210	58%		Considerable
Na_2S(A)	39	92.5%		Trace
Na_2S(B)	39	92.5%		
Na_2S(C)	39	97%		
$NaAsO_2$(A)	65	12%	78%	Trace
$NaAsO_2$(B)	65	14%	62%	Trace
$NaAsO_2$(C)	65	5%	90%	Trace

(A) Nitrobenzene added to mixture of alkali and reducing agent.
(B) Alkali added to mixture of reducing agent and nitrobenzene.
(C) Reducing agent added to mixture of alkali and nitrobenzene.

and nitrobenzene would give quite a different result. As a matter of fact, I obtained a 77 percent yield of aniline, which is identical with that obtained by the preceding method. It is impossible, at present, to tell whether this unexpected result is due to the sparing solubilities of the ferrous hydroxide and of nitrobenzene, or whether the fault is in the original premises. When ferrous sulphate was added to the hot mixture of nitrobenzene and alkali, the yield of aniline dropped to 58 percent. Considerable azobenzene distilled over with the aniline; but these experiments were made before the method for determining azobenzene and azoxybenzene had been worked out, and when I was only considering the amount of aniline formed.

Although sodium sulphide at ordinary temperatures is a weaker reducing agent than ferrous hydroxide according to the electrometric measurements, it is more efficient at higher temperatures, a yield of 92–97 percent being obtained. Since a sodium sulphide solution is strongly alkaline to start with, it was not to be expected that the addition of extra alkali would have an overwhelming effect. There does not seem to be any apparent reason why the highest yield of aniline should

be obtained when sodium sulphide is added to the mixture of nitrobenzene and alkali. It seems probable that the difference between this run and the preceding two is due to some difference in conditions which has not been recognized.

A sodium arsenite solution is also alkaline to begin with; but here we get some rather interesting differences. Sodium arsenite is a weaker reducing agent than either sodium sulphide or ferrous hydroxide, and we find that about 14 percent of aniline is the maximum yield. The other product is azoxybenzene and not azobenzene as might have been expected from the electrochemical reduction. The yield of aniline is practically the same whether nitrobenzene is added to alkaline sodium arsenite or whether alkali is added to nitrobenzene and sodium arsenite; but the yield of azoxybenzene drops from 78 to 62 percent. I am not able to offer any explanation for this.

When sodium arsenite is added to a mixture of nitrobenzene and alkali, the yield of aniline drops to about 5 percent while that of azoxybenzene rises to 90 percent. This is as it should be, though it must be admitted that these experiments have brought more problems to light than they have solved. Some of the points, however, have been cleared up by the subsequent work of Mr. H. C. Allen.

The sodium arsenite method is a particularly good one for preparing azoxybenzene. The yield is high; only traces of azobenzene are formed; and the solution, from which the azoxybenzene has to be extracted, is always clear and easy to work with.

The results of this investigation may be summed up as follows:

1. Nitrobenzene can be reduced electrolytically to aniline in ferrous chloride solution at 100° between iron electrodes. For a current density of 15 amp/dm² only 2.2 volts were needed.

2. Massive iron reacts chemically with nitrobenzene and aqueous ferrous chloride at 100°, provided the stirring is sufficiently intense to bring all these substances into intimate contact.

3. The presence of an iron salt, preferably ferrous chloride, seems to be essential. The rate of corrosion of the iron depends on the concentration of the iron salt but is not proportional to it.

4. The concentration of the ferrous chloride remains unchanged throughout the run.

5. The catalytic action of ferrous chloride is apparently due to its being a reducing agent and to its keeping the iron from becoming passive.

6. Nitrobenzene is reduced at 100° by alkaline sodium sulphide, ferrous hydroxide, and sodium arsenite solutions; but not by alkaline potassium ferrocyanide solution.

7. With sodium sulphide a yield of 92–97 percent aniline can be obtained; with ferrous hydroxide a yield of 60–80 percent aniline is obtained; with sodium arsenite the chief product is azoxybenzene, of which a 90 percent yield can be obtained.

8. It has been pointed out that theoretically we may obtain different reduction products according as we add nitrobenzene to a mixture of alkali and reducing agent, alkali to a mixture of nitrobenzene and reducing agent, or reducing agent to a mixture of alkali and nitrobenzene.

9. Experimentally, the same result was obtained with ferrous sulphate when nitrobenzene was added to alkali and ferrous hydroxide or alkali to ferrous sulphate and nitrobenzene.

10. In all cases the yield of azobenzene was very small, which is quite different from what the electrochemical experiments would have led us to believe.

This investigation was suggested by Professor Bancroft and has been carried out under his direction.

Cornell University

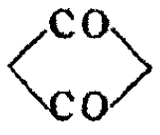
THE FLUORESCENCE OF ANTHRACENE

BY LOUISA STONE STEVENSON

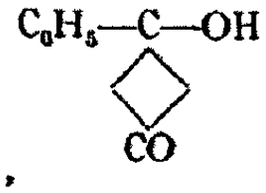
Many organic substances possess the property of fluorescence, *i. e.*, when exposed to light of a suitable wave length, they emit light of a different wave length. This phenomenon has been of interest alike to the physicist and the chemist. The physicist has examined the absorption[1] and fluorescence[2] spectra, often with a view to testing the validity of Stokes's law,[3] has studied the distribution of energy in the spectrum,[4] the photo-electric effect,[5] the effect of temperature,[6] pressure,[7] and the solvent[8] upon fluorescence. The chemist, on the other hand, has sought to establish some relation between the structure and the fluorescence of the substances. A brief account of some of these views will be given here.

Liebermann[9] gave the first rule for fluorescence in the anthracene series: "Those derivatives fluoresce in which both the carbon atoms, which join the two benzene residues possess the constitution

where M is a monovalent element or group, while those derivatives in which there is the double ketone group



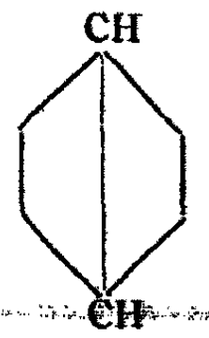
or the group, corresponding to it with phenyl anthracene,



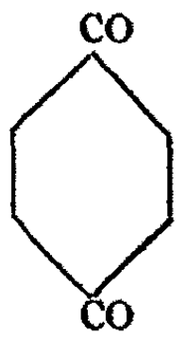
possess no fluorescence."

Buckingham[10] showed that, with the salts of eosin, β-naphthylamine sulphonic acid, and quinine, the fluorescence is due to the ions.

Meyer[11] ascribes fluorescence to certain fluorphoric groups, which often in themselves are insufficient to produce fluorescence but may effect it if they are situated between heavy atomic groups such as benzene rings. Such groups are various six-membered rings, *e. g.*, the group

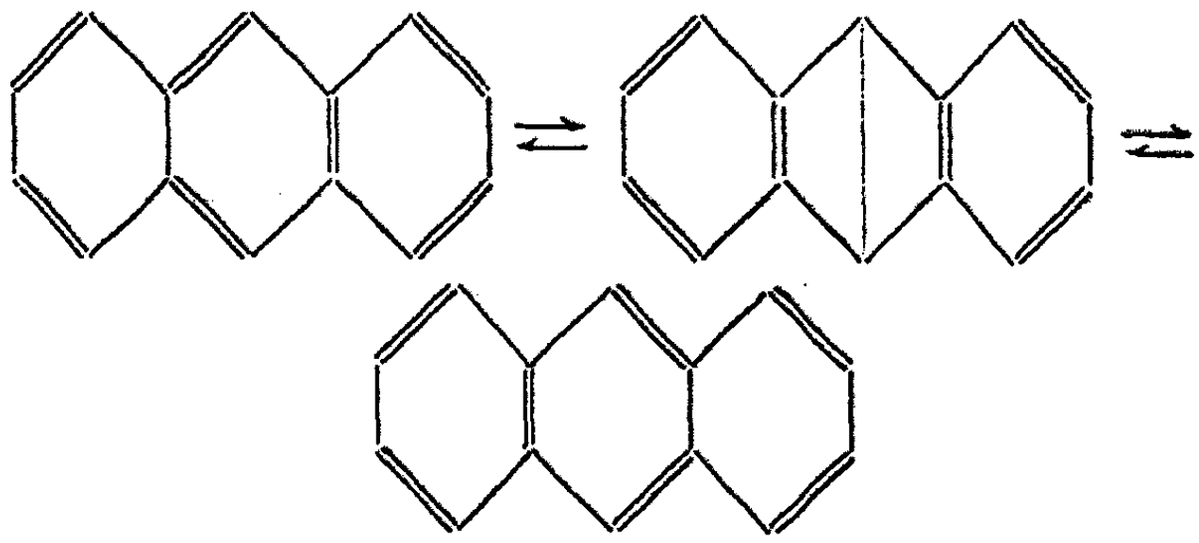


for anthracene as distinguished from the group

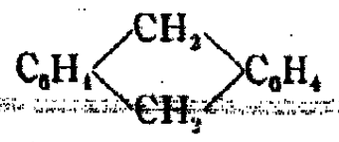


in anthraquinone, which does not allow fluorescence.

Hewitt[12] attributes fluorescence to tautomerism. Only such compounds fluoresce as are capable of existing in two isomeric forms. Light is absorbed in the formation of one and given up in the reformation of the original substance. Thus, he represents for anthracene and its derivatives the following reaction:

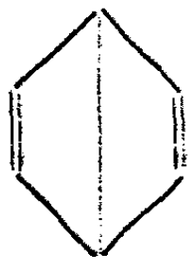


The phenomenon is like the swinging of a pendulum between the two end positions (forms) which are the same. Such derivatives of anthracene should fluoresce as have the structure represented by the central formula. This theory has never met with entire acceptance. Whereas it is possible that in some cases fluorescence may accompany tautomeric change, the above represented tautomeric change cannot account for fluorescence in the anthracene series. It does not account for the fluorescence of dihydroanthracene.



which does not have the central bond of union, necessary according to the above explanation.

Kauffmann[13] has studied the luminescence of vapors of many organic substances when they are excited by Tesla waves. The same color of light is given off when these substances, as solids, are exposed to radium emanations. Some of these substances are not fluorescent although some of their derivatives are. Others are fluorescent and, of these, all give the same color whether in fluorescence or when excited by Tesla waves or radium emanations. Kauffmann therefore regards the carbon-containing ring in all these substances as a *luminophore*, which possesses the property of being excited into luminescence by Tesla waves but not by light. Certain auxochromic groups as NH_2 or OH, when substituted in these compounds cause fluorescence and also cause benzene to behave according to the Dewar formula:



Therefore, he concludes that the Dewar benzene ring is the luminophore, into which various *fluorogenic* groups are substituted before fluorescence appears. This view reminds one of Meyer's and Hewitt's views concerning the fluorescence

of the anthracene molecule. The main difference is that Kauffmann emphasizes the fact that it is the parallel double bonds and not the para-union, which is effective here. This view would include anthraquinone among the fluorescent substances as it also possesses the parallel double bonds.

Stark[14] has later demonstrated the ultraviolet fluorescence of benzene. These theories would then have to be modified so that the benzene ring stands as *fluorophore* and the substituting groups are *auxofloric* or *hypsofloric* in their character according as their substitution in the ring shifts the fluorescence towards or away from the visible spectrum.

Miss Woker[15] has collected a great many data, concerning the fluorescence of substances, belonging to the same groups. She, too, regards fluorescence as dependent upon certain groupings in the molecule and gives rules with regard to the inhibiting effect of substitution upon fluorescence. Fluorescence may be destroyed when a chromophoric group is introduced into the molecule, either through the production of a color complementary to the fluorescence or through displacement of the absorption bands toward the red end of the spectrum. Substitution of salt-forming groups in the molecule is often destructive to fluorescence because the absorption bands are pushed toward the red end of the spectrum or because the coloring effect of the chromophore is reënforced. Again, the latent fluorescence, which is present in simple benzene derivatives, may be increased by substitution of salt-forming groups for again the absorption bands are pushed toward the red, *i. e.*, into the visible spectrum.

All this work while it has emphasized the general relations between organic substances which fluoresce, has yet not shown the underlying cause of the fluorescence. As far as fluorescence in the anthracene series is concerned, all are agreed that the fluorescence is connected with the meso-ring of the anthracene molecule.

As with general investigation on fluorescence, so with its explanation, there are two theories, a purely physical theory and a chemical theory.

Physical Theories

In fluorescence, light of some given wave length is absorbed and light of a different wave length is emitted. As in the ordinary light phenomena, such as reflection, refraction, dispersion, there is no evidence of change of wave length, we must assume here some intermediate stage. Lommel[16] replies that fluorescence is due to resonance and is analogous to sound vibrations. The molecules or parts of molecules are set in vibration if they possess a period sufficiently like that of the exciting light. Like the swinging of a pendulum, acted upon by an outside force, the molecule or its part vibrates with a period of its own and also with a period forced upon it. Therefore the wave length of maximum intensity of the fluorescent spectrum should be dependent not only on the constitution of the molecule but also upon the wave length of the exciting light. It has been shown by Schmidt,[17] also by Nichols and Merritt,[18] that this is not true for certain fluorescent substances, with which the position of the maximum of fluorescence remained constant with varying exciting light. A simple resonance explanation, therefore, does not suffice.

Stark[19] has devised a more elaborate theory, which includes the assumption either of free or loosely bound electrons. His belief in these is based on the fact that he has found that many organic substances which fluoresce exhibit the photoelectric effect, *i. e.*, when negatively charged, they give off negative electrons in the presence of light. Fluorescence and photoelectric effect, says Stark, are intimately connected with absorption bands, which are shaded toward the red. The carriers of the band spectra are negative electrons, which are displaced from their normal position by the incident light and on return to the molecule, they give out light. If the separation of the negative electrons is complete, then the photoelectric effect occurs. Thus he explains the fluorescence of solid anthracene, *a*-anthrol, and *a*-methyl anthracene. Fluorescence then always accompanies the photoelectric effect. However, the converse is

not true, for a change in the union of the valence electron may take place, which is sufficient to cause fluorescence without setting the electron free from the sphere of action of the atom or the molecule. The time of fluorescence is practically identical with the period of excitation because the loose valence electrons have very small mass and their reaction velocity is proportionally great. Furthermore, the fluorescence of a benzene derivative may be made latent by a chromophoric group if the absorption spectrum of the chromophore is in the same position as the emission spectrum of the fluorescent light of the benzene derivative. Although fluorescence is latent, we may get the photoelectric effect, which accompanies that latent fluorescence. Such is the case with anthraquinone, which shows no fluorescence under ordinary circumstances, but does have a photoelectric effect.

It is difficult to reconcile with this theory the results of Howe[20] concerning the electrical conductivity of fluorescent anthracene vapor. He finds that this vapor possesses no different conductivity from non-illuminated anthracene vapor. This does not seem to be in accord with what we would expect if the fluorescence of anthracene is due to the return of negative electrons to the molecule.

Furthermore, Schmidt[21] has shown with solid fuchsine, methyl violet, eosin, malachite-green and their solutions, that fluorescence, ionization, and photoelectric effect do not coincide. The photoelectric effects seem to be the same whether ionization and fluorescence are great or small.

Chemical Theory of Fluorescence

The chemical view of fluorescence, on the other hand says[22] that the light causes some chemical reaction to take place. Either light is given off during this reaction, or during the reverse reaction or during both. Expressing this in a simple way, we may say:

(1) $A + \text{light} \longrightarrow B + \text{fluorescence}$
$B \longrightarrow A$
(2) or $A + \text{light} \longrightarrow B$
$B \longrightarrow A + \text{fluorescence}$

(3) or A + light ⟶ B + fluorescence
B ⟶ A + fluorescence.

Phosphorescence is explained in a similar way, only here the reverse change is a slower one so that there are often visible traces of decomposition. Wilkinson[23] has explained the phosphorescence of inorganic salts under the influence of cathode rays in such a way and has presented evidence of the products of decomposition.

The purpose of this investigation was to see if such a theory may be used to explain the fluorescence of anthracene and its derivatives.

Anthracene itself fluoresces both as solid and vapor as well as in solution. Nichols and Merritt[24] have studied the fluorescence of anthracene at the temperature of liquid air, when excited by an arc between magnesium terminals, and have found that it has undiminished fluorescence at that temperature. A list of some of the more common fluorescent derivatives of anthracene is given below, together with the position of the substituting groups, where they are known, and the color of the fluorescence:

Name	Position of substituting groups	Fluorescence (in solution)[1]
Monochloranthracene	9	blue
Anthracenedichloride	9–10	blue[1]
Dichloranthracene	9–10	blue
Dichloranthracene dichloride	9–10, 9–10	blue
Dichloranthracene tetrachloride		blue-slight
Trichloranthracene		green
Tetrachloranthracene		green
Octochloranthracene		green
Dihydroanthracene	9–10	blue
Dibromanthracene	9–10	blue
Tribromanthracene		blue
Phenylanthracene	9	blue
Phenylanthracene dihydride	9 9–10	blue
Isobutylanthracene	9	fluorescing needles (solid)
Isoamylanthracene	9	blue
Methylanthracene	2	blue (solid)
Trimethylanthracene	1–4–6	blue-green (solid)
Benzylanthracene	9	blue

[1] The chlorine substitution and addition products were made and their fluorescence tested in cases where they were not listed as fluorescent.

Name	Position of groups	Fluorescence
Anthrol	1	blue (solid)
Anthrol	2	blue (solution)
Oxyanthranol dihydride	1–10–OH	green-yellow
	9–10–H	
Dioxyanthranol		green-blue
Anthranol	9–OH	blue (solution)
Anthranol dihydride	9–9–10	blue (solution)
Aminoanthracene	9	green(solution)
Aminoanthracene	2	green(solution)
Acetyl derivative		blue (solution)
Formyl derivative		green(solution)
Anthracene monocarboxyl acid	9	blue (solution)
Sodium salt		
Amide		blue
Chloride		green
Methyl and ethyl ethers of oxanthranol	O–9	
	H } 10	
	OH }	blue

None of the derivatives, which contain two CO groups in the meso-ring although some which contain one such group, are fluorescent. Two monovalent atoms or groups may be attached to the meso-carbon atoms and still have fluorescence as is indicated by the fluorescence of dichloranthracene dichloride and dihydroanthracene. The fluorescence, then, as others before have noted, is concerned with the meso-ring of anthracene. Moreover, the presence or absence of the para-bond has nothing to do with it, since, of the derivatives of anthracene which fluoresce, some have the para-bond and others do not have it.

Let us now consider what may take place during the action of light and fluorescence. Fluorescence may take place if any of the following conditions are fulfilled:

(I) A reaction, which is giving off light in the invisible spectrum or which is giving off light of small intensity in the visible spectrum, is taking place all the time. The incident light then either causes sufficient change of wave length to bring the emitted light into the visible spectrum or else accelerates the reaction sufficiently so that visible light is given off.

(II) In the presence of light, there is a change from one form to a second tautomeric form. Light is given out during the formation of the second substance or during the reformation of the first or during both.

(III) The light causes a dissociation. Either in the dissociation or in the reassociation of the parts of the molecule, light is evolved. This dissociation may be ionic or non-ionic in its character.

Experimental Work

Experiments were then made to see with which of these three cases we are dealing with anthracene and its derivatives.

Case I

Here the photographic method was used to detect any light, which might be given off.

(1) Benzene and toluene solutions of dihydroanthracene, dichloranthracene, dibromanthracene, all of which are very fluorescent, were allowed to stand in the dark as close as possible to the photographic plate. In some of the experiments, the solutions were contained in glass test tubes. Finally, although the fluorescence is visible through glass, quartz vessels were used in order not to cut off any ultraviolet light. A Σ Lumière fast plate was used and was developed with the solution, recommended by Perley.[25] The time of exposure was varied from three hours up to forty-eight hours but in no case was any impression obtained on the plate.

(2) The following other solutions were tried to see if other fluorescent substances gave off light in the dark: These experiments also gave negative results.

Solution used	Time of exposure	Material of container
Alcoholic eosin	24 hours	glass
Alcoholic fluoresceïn (trace of alkali)	24 hours	glass
Alcoholic fluoresceïn	41 hours	glass
Quinine sulphate (alc.)	41 hours	glass
α-Naphthylamine in alcohol	48 hours	glass
Quinine sulphate in alcohol	48 hours	quartz

(3) A reaction, which is known to give off light was now used to test this photographic method. LeBon[26] and later, Miss Gates[27] have studied the evolution of light from hydrated quinine sulphate and have shown that light is evolved when the salt is dehydrated and also when it takes up water again. If on slow dehydration, the same amount of light is given off, we shall expect in accordance with Bunsen and Roscoe's law, to get the same chemical effect.

Experiments

(1′) The hydrated quinine sulphate was placed in one arm of a U-tube such as is used for making a standard cell. In the other arm of the tube was placed concentrated sulphuric acid. The U-tube was closed, placed in a plate-box with a Σ plate and left for a week. On development of the plate, no image was found.

(2′) Two small test tubes, the one inside the other were used. Between them was placed a thin layer of the hydrated salt. In the inner tube was concentrated sulphuric acid. The outer tube was corked and the combination was exposed to a Σ plate for a week and again with no result.

(3′) A more powerful dehydrating agent, phosphorus pentoxide, was substituted for the sulphuric acid and experiment (2′) was repeated. An absolutely clear negative was obtained.

(4′) Experiments (2′) and (3′) were repeated with exposures of a month's time in each case. Even then, the plate showed no evidence that light had been given off.

With rapid dehydration as by heat, Miss Gates obtained visible light. I, myself, have obtained very satisfactory results, using the same apparatus and plates, in photographing the light given off in dehydration when a few drops of concentrated sulphuric acid are allowed to fall on the hydrated quinine sulphate. The light is sufficiently visible in a dark room so that the position of the tube can readily be located.

(5′) It may be possible that the wave length given out in dehydration is different when the dehydration is slow from that which is given out when dehydration is rapid. If this

is so, there should be a gradual change in the light evolved when sulphuric acid, containing varying amounts of water, is added to the hydrated salt. This experiment was tried. The intensity of the light diminished as sulphuric acid, containing more and more water, was added to the separate portions of hydrated quinine sulphate. No change in the color of the light could be detected. Moreover, the experiments of Nichols and Merritt,[18] who found that, with varying wave length of exciting light, there was no change in the position of the wave length of maximum intensity of fluorescent light, make a shifting of the wave length of the light given off by quinine sulphate less probable.

We must therefore conclude that in the slow dehydration of quinine sulphate, the intensity of the light given off is so small that the effect on the photographic plate is *nil*.

As far then as the fluorescent solutions are concerned, we have only shown that no light of sufficient intensity to affect the photographic plate is evolved.

These experiments are of interest with a view to the work of Luther and Weigert[28] on the transformation of dianthracene into anthracene. They report that this change is unaccompanied by light as tested by the photographic method. In this case, too, the change may be so slow that the photographic method is at present not sufficiently delicate to detect it. The same may also be said of the transformation of the so-called insoluble sulphur into soluble sulphur, studied by Bancroft[29] and Rankin.

Case II

That the fluorescence of anthracene cannot be due to a tautomeric change, which involves the shifting of the meso-linkage has already been shown; for compounds, such as dihydroanthracene, which do not contain the para-bond, fluoresce. There still remains the possibility that the H atoms or the groups, which substitute these atoms in the case of the derivatives of anthracene, shift from the middle ring and form some tautomeric addition compound by attaching themselves to the side-ring. This is probably not the case

as can be seen by a study of the chlorine derivatives of anthracene. If there is a position in the side-ring, which is peculiarly susceptible to the formation of addition products, such a position should be taken by chlorine when it adds to the molecule. When chlorine is added to γ-dichloranthracene, the first two chlorine atoms are added to the middle ring, then two more are added, which must necessarily be added to the side-ring. The dichloranthracene tetrachloride thus formed is fluorescent. This substance could not be fluorescent, if, by its formation, *i. e.*, by the addition of the chlorine atoms in the side-ring, those positions in the molecule had been occupied which formerly were occupied during fluorescence of dichloranthracene by chlorine atoms, which shifted from the meso-ring during tautomeric change. Therefore, it is probable that such a tautomeric change does not take place for, on the assumption of such a change, dichloranthracene tetrachloride should be non-fluorescent.

Case III

It remains now to decide whether the fluorescence of the anthracene group is due to dissociation. That such a dissociation is not an ionic one has been shown by Howe[20] in his experiment on the conductivity of fluorescent anthracene vapor.

If then dissociation takes place, it must be of such a nature, that the part dissociated does not carry an electric charge. The simplest assumption that may be made is that, under the influence of light, the hydrogen atoms or whatever monovalent substituting groups replace these atoms are dissociated from the meso-position in the molecule. Either the dissociation of these groups or the reassociation of them with the molecule must then be accompanied by the evolution of light.

If the reassociation takes place with evolution of light, we should be able to reproduce this light, *i. e.*, we may put together the two parts of the molecule and see if light is evolved. If anthracene is treated with chlorine, hydrochloric acid is evolved and γ-dichloranthracene, one of the

most fluorescent of the anthracene compounds, is formed. At the moment when chlorine enters the molecule, we have the union of the residue of the molecule and the chlorine atom. If therefore the fluorescence of dichloranthracene is due to light given out when the dissociated chlorine atoms reunite with the carbon atoms of the middle ring, light should also be given off by the action of chlorine upon anthracene. This reaction was tried.

Experiment

The anthracene was heated in a 500 cc flask until the thermometer in the center of the flask showed a temperature of 213° C, the melting point of anthracene. The experiment was performed in a dark room at night. When the required temperature was reached, the flame was removed and chlorine was run immediately into the flask. Sufficient light is given off so that the shape of the flask can be plainly seen in the dark room. The light appeared to be bluish-white. It appears then that the assumption made concerning the fluorescence of dichloranthracene has experimental basis.

Stark[30] has noted the identity of the fluorescence spectra of *a*-methyl anthracene, *a*-hydroxyanthracene (*a*-anthrol) and anthracene. From this, he concludes it is evident that ultraviolet light partially decomposes the first two named substances into anthracene. This does not seem to be a necessary conclusion. It would be simpler to regard the substituting groups CH_3 and OH as having no effect on the fluorescent spectrum as might easily be the case if the light in this spectrum is caused by reassociation of the hydrogen atoms with the middle ring.

Kauffmann[31] reports that under the influence of Tesla rays, vapors of anthracene, dichloranthracene and dihydroanthracene, give a blue light while vapors of anthraquinone are not excited by these rays. The β-rays from radium produce a similar effect. We are evidently dealing here with a similar phenomenon to that of fluorescence and probably the cause of it is the same.

At high temperatures or with very energetic bombard-

ment as in a cathode-ray tube, Wiedemann and Schmidt[33] have reported fluorescence for anthraquinone. This is the only case where I have found anthraquinone listed as luminescent at all. They give the following results for anthracene and anthraquinone:

I. Fluorescence of the vapor in an evacuated sealed tube:
Anthracene—blue.
Anthraquinone—blue.

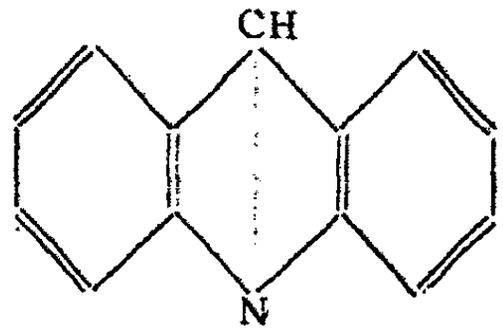
II. Electro-luminescence—*i.e.*, the lighting of the dilute vapors under the influence of the charges from a Holz machine or an induction coil.
Anthracene—bright blue.
Anthraquinone—green-blue.

III. Cathodo-luminescence of the solids:
Anthracene—green—no after lighting.
Anthraquinone — green-yellow — bright phosphorescence, which fades quickly. No thermo-luminescence.

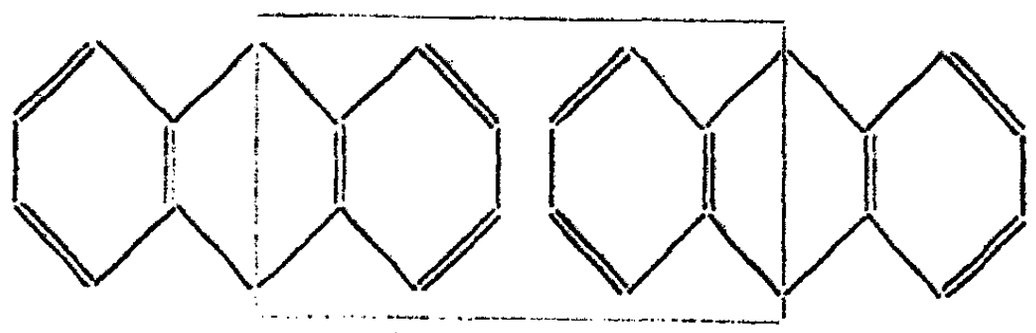
Here conditions are reached in which probably dissociation takes place with anthraquinone as well as anthracene.

The Dianthracene Formation

As is well known, anthracene is transformed very readily in the presence of light into dianthracene.[33] Certain derivatives, undergo a similar change, *e. g.*, β-methyl anthracene[36] and anthranol.[34] Probably also, acridine[35] which has a similar constitution is converted



into a corresponding polymer. The structure of dianthracene is believed to be represented in this way



although it has not been proved absolutely. We only know definitely that it is a double molecule. As the formation takes place only in the light, this reaction has been regarded as having an intimate connection with the fluorescence of anthracene.

According to our view of the fluorescence of anthracene, it hardly seems possible that such a connection exists. If it becomes easier for two anthracene molecules to unite by the joining of the meso-bonds, when the hydrogen is dissociated from the molecule for an instant under the influence of light, we would expect that similarly from γ-dichloranthracene, we would obtain a dichlordianthracene. Attempts to make this substance have not been successful.[17] The substances, which have given polymers have been those in which substituting groups were in the side-rings or only one substituent in the middle ring. Another reason, which makes us skeptical concerning the connection between fluorescence and dianthracene formation is that derivatives of anthracene possess strong fluorescence, which do not contain the para-bond of union, and therefore cannot form dianthracene derivatives. Since then the fluorescence of anthracene derivatives does not depend upon the presence of the para-bond, whereas dianthracene formation does depend upon it, it is doubtful if there is any connection between the fluorescence of anthracene and the dianthracene formation.

Byk[38] has offered an explanation, which is based on Thiele's[41] theory of partial valences and on the photoelectric effect of anthracene. This again is not very satisfactory, especially when we recall the fact that anthraquinone also has a photoelectric effect.

It is interesting to note in connection with dianthracene that Nichols and Merritt[39] have reported a fluorescence of 2 at 18° C, and a fluorescence of 4 at the temperature of liquid air as compared with a fluorescence intensity of 4 for anthracene. This is in contradiction to other observers, who have reported dianthracene to be non-fluorescent. The fluorescence at 18° C is undoubtedly due to the presence of

some anthracene as impurity but the increase in fluorescence at the lower temperature cannot be due to this cause as anthracene has the same intensity of fluorescence at low temperatures as at room temperatures.

Oxidation of Anthracene in the Light

If in the presence of light, the hydrogen atoms are dissociated from the middle ring of anthracene, we may find that some of the chemical reactions, which affect that middle ring are light-sensitive. Anthracene is quoted[40] as being much more sensitive to reactions when in fluorescent condition and especially in the presence of oxygen. It was therefore decided to make a study of the oxidation of anthracene in the presence and absence of light. Here no oxidizing agent such as $KMnO_4$ or CrO_3, which will exercise strong selective absorption can be used.

(1) In the first place, oxygen at room temperature was passed through a benzene solution in the sunlight for three days. No oxidation took place here. This was proven by the absence of the characteristic red color of oxanthranol, when the residue, after the evaporation of the benzene, was tested for anthraquinone by warming it with zinc dust and caustic soda solution.

(2) Then the vapor was oxidized. At temperatures above 200° C, anthracene reacts with oxygen with explosive violence even in the dark. The formation of anthraquinone can be detected at temperatures as low as 140°–150° C both in the light and in the dark. Below this temperature, no anthraquinone was found. As before, the formation of oxanthranol was used as test for anthraquinone.

Thus results up to the present time have not shown the anthracene molecule to be more sensitive to chemical reaction in the light than in the dark. If, indeed, it is, the range of this sensitiveness is very small and very careful experiments must be made to detect it.

This oxidation reaction was probably not a happy choice for it is complicated in two ways. In the first place, at the temperature of the experiment, much of the anthracene is

transformed into dianthracene. In the second place, in this oxidation, we are dealing with two things: (1) the dissociation of the hydrogen atoms through fluorescence, (2) the breaking of the para-bond, which must occur before anthraquinone is formed. Whereas the first is a light-sensitive reaction, the breaking of the para-bond may not be. This might easily mask the light-sensitiveness of the first reaction. It would have been better to try here the oxidation of dihydroanthracene, from which both (1) and (2) are excluded. This will be tried at a later date.

The Chlorination of Anthracene

In connection with the study of the chemical reactions of anthracene, we desired to know the effect of chlorination in the dark and the light, in the presence and absence of carriers. No record of such experiments could be found and so the work was done here.

Experimental

The anthracene used was a C. P. grade, which melted at 213° C but was not absolutely pure as it was colored yellow, due probably to traces of chrysogen as impurity. Carbon tetrachloride solutions containing 10 percent anthracene were used for these experiments. The initial temperature was room temperature and was not varied except in so far as the heat due to chemical reaction or exposure to the direct rays of the sun changed it. The experiments in the light were made in the direct sunlight during the spring and early summer. Those run in the dark were made in a dark hood and the flask containing the anthracene solution was wrapped with a black cloth. Three corresponding experiments were tried in the light and in the dark:

I. Chlorination in the absence of a carrier.
II. Chlorination in the presence of iron filings.
III. Chlorination in the presence of red phosphorus.

The results of these experiments are given below:

A. Chlorination in the dark

Conditions	Percent Cl in product	Theor. percent	Name
I	28.86	28.70	Dichloranthracene
II	53.25	54.71	Dichloranthracene tetrachloride
III	66.26	67.31	Hexachloranthracene tetrachloride

B. Chlorination in the light

Conditions	Percent Cl in product	Theor. percent	Name of product
I	67.21	67.31	Hexachloranthracene tetrachloride
II	66.25	67.31	Hexachloranthracene tetrachloride
III	66.97	67.31	Hexachloranthracene tetrachloride

The analyses for the product obtained run low here for two reasons:

(1) In all cases the product was contaminated with an oil, which was difficult to remove completely though it was removed to a large extent by washing with ether.

(2) In the case of addition products, except in Case B, I, the solid which precipitated from the carbon tetrachloride, was contaminated with small bits of iron filings and red phosphorus. These could not be easily removed as crystallization from hot solvents tends to decompose the addition products which are relatively insoluble in the cold solvents.

The results obtained agree in general with results which have been obtained on the chlorination of benzene and toluene. They are therefore in agreement with Bancroft's[42] theory of halogen carriers. If we compare with benzene, chlorination in the ring is equivalent to chlorination in the meso-ring in the anthracene molecule. Chlorination in sunlight and in the presence of phosphorus in the dark are identical and result in substitution in the side benzene nucleus and addition and substitution in the middle and side rings. It is interesting to note that iron filings, which are regarded as an excellent halogen carrier, have no effect in the further

substitution of chlorine but in their presence, four chlorine atoms are added to the anthracene molecule in the dark.

Of the products obtained, the only one, which has not been previously described, is the hexachloranthracene tetrachloride. This, like all the other chlorine addition products of anthracene, is a white solid, which melts under evolution of HCl and is relatively insoluble in carbon tetrachloride.

Summary

(1) A partial review of the work done on the fluorescence of organic compounds has been given.

(2) A theory has been given to account for the fluorescence of anthracene and its derivatives.

(3) This theory accounts for all known fluorescent anthracene derivatives and finds support in the evolution of light, which takes place when chlorine acts upon anthracene in the formation of dichloranthracene.

(4) The luminescence of anthracene when excited by Tesla rays or the β-rays of radium may be accounted for in a similar way.

(5) This theory does not show any connection between the fluorescence of anthracene and the dianthracene formation.

(6) In the dark, solutions of certain fluorescent substances do not give off any light, which can be detected by the Σ Lumière plate.

(7) The dehydration of quinine sulphate, a reaction which gives off light, may take place so slowly that no light can be detected by the use of the Lumière plate.

(8) The phenomenon noted in (7) is probably not due to a change in the wave length of the emitted light.

(9) The oxidation of anthracene vapor by gaseous oxygen is not a reaction, which is sensitive to light.

(10) The chlorination of anthracene has been studied. In the dark, dichloranthracene is formed. In the dark in the presence of iron filings, dichloranthracene tetrachloride is formed. In the dark in the presence of phosphorus, and in

the light with and without a carrier, hexachloranthracene tetrachloride is formed.

This work was suggested by Professor Bancroft and was carried out under his supervision. The author takes this opportunity to acknowledge her indebtedness to him for many suggestions and to express her appreciation of his generous interest in the work.

Cornell University,
May, 1911

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A NEW AND SIMPLE METHOD FOR COMPARING MOLECULAR WEIGHTS

BY PHILIP BLACKMAN

Part I

Theory.—If equal weights of two substances, whose molecular weights are respectively m_1 and m_2, be dissolved in equal volumes of the same solvent, at like temperature, and v_1 and v_2 be their respective "molecular velocities" in solution, then

$$m_1 v_1^2 = m_2 v_2^2,$$

or

$$\frac{m_1}{m_2} = \frac{v_2^2}{v_1^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1).$$

Consider these two solutions connected by (or separated by) the same solvent, all maintained at the same temperature, and that the respective molecules can travel only in a linear, horizontal direction towards each other; after a time t the molecules will meet, and the respective distances traveled will be given by the equations

$$d_1 = v_1 t,$$

and

$$d_2 = v_2 t;$$

thus

$$\frac{v_2^2}{v_1^2} = \frac{d_2^2}{d_1^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

Combining equations (1) and (2) we obtain the necessary working formula

$$\frac{m_1}{m_2} = \frac{d_2^2}{d_1^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3).$$

Apparatus.—The apparatus consists of a straight, uniform, fairly wide (3–4 mm diameter bore) glass tube, having at each end, at right angles to the tube, a cup with a wide mouth. A ground glass, globular bead closes the ground neck of each cup, and the mouths can be closed by means of rubber stoppers, Fig. 1.

Method.—The substances, whose molecular weights are to be compared, must be so chosen that, when they come in contact in solution, they produce a distinct coloration or preferably a precipitate. They are weighed out in equal quantities and dissolved in equal volumes of the same solvent (sufficient solvent being used to give very dilute solutions).

Fig. 1.

The beads are removed, and, the apparatus being kept level, the tube is filled with the solvent, the beads are replaced, and any liquid remaining in the cups completely removed by aid of blotting or filter paper. The two cups are then filled *quite to the brims* with the respective solutions (the beads thus prevent the admixture of the specifically heavier solutions with the connecting liquid in the tube), and the mouths are closed with rubber stoppers, care being taken that no air is enclosed (the cups, if of the shape shown, and *completely filled to the brims*, will facilitate the exclusion of air bubbles). Any solutions remaining round the stoppers near the brims may be wiped away. The apparatus is now inverted, keeping the tube in a horizontal position and free from vibration; the beads fall down upon the stoppers, and thus connection is obtained between the two solutions, Fig. 2. The apparatus is left for diffusion to take place. When the dissolved bodies have met within the tube, the precipitate or color, as the case might be, is produced. The formation

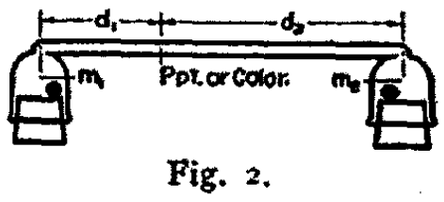

Fig. 2.

of a precipitate would to a great extent prevent further diffusion, but the production of a color would not necessarily prevent further diffusion and increase in the extent of the color. The respective distances d_1 and d_2 are measured from the junctions of the cups and tube to the precipitate or color. As the process of diffusion takes place at a very slow rate a

very considerable time (twelve hours or more) may elapse before any result can be observed.

Results.—Experiments were carried out with silver nitrate [$(AgNO_3]m_1 = 170$) and sodium chloride [$(NaCl]m_2 = 58.5$) in aqueous solution. The mean for ten successful determinations gave $d_2^2/d_1^2 = 3.0$, whereas theoretically $m_1/m_2 = 2.9$.

Remarks.—It will be observed that the bulbs or cups are directly seated upon the tube, thus there being no bends or necks and the solutes therefore not having to diffuse in an upward vertical direction but doing so in a linear horizontal direction only.

Messrs. Townson & Mercer, 34 Camomile St., London, E. C. (England), manufacture and supply the apparatus.

London

A NEW METHOD FOR DETERMINING VAPOR DENSITIES

BY PHILIP BLACKMAN

Part IX[1]

The following apparatus will be found much more expensive than the modified apparatus described in the Journal of Physical Chemistry, **12**, 691–692 (1908), or *Berichte der deutschen chemischen Gesellschaft*, **42**, 4142 (1908), but it will be found to possess this great advantage, *viz.*, the apparatus will admit of being heated to high temperatures; like that apparatus above mentioned, and unlike all others described, it does not require a complicated arrangement of heating jacket, condenser, etc., with all their necessary attendant supporting apparatus such as most other vapor density methods require, and also it occupies a comparatively small bulk. It is most useful when a quick, but not too accurate, result is required; it is not so accurate as the other apparatus described by the author in Parts I–VIII because, on account of the comparatively large width of the measuring tube, it would be practically impossible to subdivide conveniently the volume-calibrations beyond half cubic centimeters.

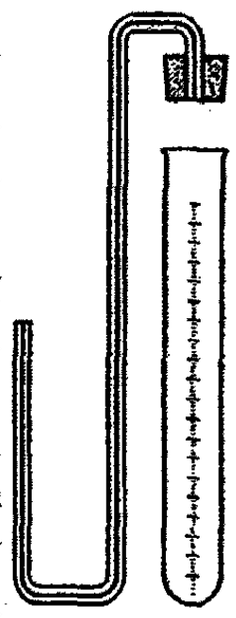

Fig. 1.

The apparatus consists of a glass measuring tube, fairly thick-walled, about 15–20 cc in length, and 25 mm (circa) in internal diameter, calibrated in cc and half cc, the calibrations and figuring to begin from the closed end. The mouth has a rim or lip, the neck is ground for a short distance on the inside, and a well-ground glass stopper with a glass capillary tube (of fairly wide bore) of the shape shown in Fig. 1 fits into it.

It is advisable to use a specially prepared glass-stoppered weighing bottle of the shape and size (approximate) shown

[1] Continued from the Journal of Physical Chemistry, **13**, 433 (1909); Chemical News, **101**, 121 (1910).

in Fig. 2 (supplied by Messrs. F. E. Becker & Co., Ltd., 17–27, Hatton Wall, London, E. C.); the ordinary vapor density bottles are of such a length that they will not easily lie across the tubes along the mercury, and may jam in the measuring tubes.

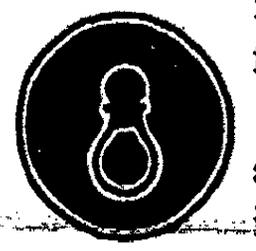

Fig. 2.

Two long pieces of soft copper wire ($^1/_{16}$ inch diameter will do well) are twisted together to form a loop in the middle.

The tube is filled with clean, dry mercury, all air bubbles are removed, the stoppered weighing bottle (filled with the known weight of the body to be experimented on) is placed upon the mercury, and the stopper forced inwards, whereby the weighing bottle is forced inwards and the surplus of mercury fills the capillary tube and further excess escapes. The looped wires are passed over the stopper round the capillary tube, and the ends drawn round the tube in opposite directions and twisted together, this operation is repeated several times, whereby the stopper will be held firmly in position, and at the same time the ends of the wire on being twisted together will form a convenient means for suspending the apparatus. Care must be taken to twist the wires always in one direction, otherwise they will be unwound in one place while being fastened in another. The apparatus is suspended by means of the wire, as already mentioned, in an inverted position, within a large, deep beaker, and heated in some convenient heating medium (water, glycerol, paraffin wax, etc.), to the desired temperature (see Fig. 3).

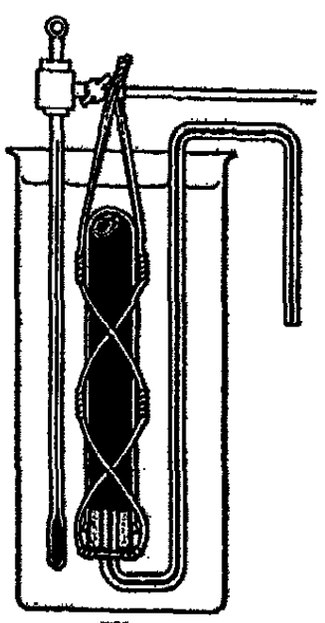

Fig. 3.

Hackney Technical Institute, London,
June, 1910

A SIMPLE METHOD FOR VAPOR DENSITY DETERMINATIONS

PART XI.[1]—THE DEHYDRATION OF COPPER-SULPHATE PENTAHYDRATE

BY PHILIP BLACKMAN

The bulbs were heated in a thermostat, wax being the heating medium, but no protective outer jacket was employed. The results of the experiments here detailed would seem to show that the evolution of water from the $CuSO_4.5H_2O$ was a function of the temperature and pressure and does not take place in the evolution of only whole molecules, and consequently the dehydration is comparable to the removal of water from an ordinary aqueous solution of a substance, or to the decomposition by heat of other molecular compounds such as acetaldehyde, ammonia, phosphorus, pentachloride, ammonium chloride, chloral hydrate, etc.

The weight of water w given off at any temperature is calculated from the formula

$$w = \frac{dpVL(L_c - l)}{31068\, l\, L_c(273 + t_1)}$$

(where d = the vapor density of water = 9), and the corresponding internal pressure (atmospheres) π of the bulb from the formula

$$\pi = \frac{pL_c(273 + t_2)}{760\, l(273 + t_1)}.$$

The molecular weight of $CuSO_4.5H_2O = x = 249.66$; the molecular weight of $5H_2O = y = 90$; hence the proportion of water in weight c of copper sulphate $= cy/x$; therefore the proportion, h, of water evolved from the hydrate $= xw/cy$, and consequently the corresponding number of molecules is $5h$.

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[1] Continued from the Journal of Physical Chemistry, 13, 431 (1909); Chemical News, 100, 174 (1909); Zeitschrift für physikalische Chemie, 65, 552 (1909).

EXPERIMENT I

c = 0.0582 gram; L_c = 194 mm; L_{cc} = 212 mm; p = 765 mm; t_1 = 10.5° C; V = 22.4 cc

t_2°	l mm	w gram	π atmospheres	h	5 h
85	177	0.0032	1.39	0.15	0.7
90	172	0.0037	1.45	0.18	0.9
95	158	0.0055	1.60	0.26	1.3
100	145	0.0074	1.77	0.35	1.7
105	136	0.0089	1.91	0.43	2.1
110	130	0.0101	2.03	0.48	2.4

EXPERIMENT II

c = 0.0448 gram; L_c = 187 mm; L_{cc} = 206 mm; p = 765 mm; t_1 = 10.5° C; V = 33.7 cc

t_2	l	w	π	h	5 h
85	176	0.0036	1.10	0.22	1.1
90	171	0.0043	1.44	0.26	1.3
95	159	0.0062	1.53	0.38	1.9
100	150	0.0076	1.64	0.50	2.5
105	139	0.0100	1.80	0.62	3.1
110	135	0.0110	1.88	0.68	3.4

EXPERIMENT III

c = 0.0418 gram; L_c = 179 mm; L_{cc} = 203 mm; t_1 = 13.5° C; p = 767 mm; V = 30.3 cc

t_2	l	w	π	h	5 h
80	169	0.004168	1.31	0.28	1.3
85	167	0.004466	1.35	0.29	1.4
90	157	0.00607	1.46	0.40	2.0
95	144	0.00849	1.61	0.56	2.8
100	139	0.00954	1.69	0.63	3.1
105	135	0.01043	1.77	0.69	3.4
110	133	0.01090	1.82	0.72	3.6
115	131	0.01138	1.87	0.75	3.7

EXPERIMENT IV

c = 0.0613 gram; L_r = 192 mm; L_c = 211 mm; t_1 = 13.5° C; p = 767 mm; V = 20.5 cc

t_2	l	w	π	h	$5h$
80	179	0.00261	1.33	0.12	0.59
85	177	0.00280	1.37	0.13	0.63
90	163	0.00430	1.51	0.19	0.97
95	153	0.00553	1.63	0.25	1.25
100	145	0.00665	1.74	0.30	1.50
105	132	0.00874	1.94	0.39	1.97
110	126	0.00985	2.056	0.44	2.22
115	120	0.01107	2.187	0.50	2.50

EXPERIMENT V

c = 0.1034 gram; L_r = 244 mm; L_c = 262 mm; p = 755 mm; t_1 = 12.5° C; V = 40.5 cc

t_2	l	w	π	h	$5h$
80	225	0.0047	1.13	0.13	0.6
90	214	0.0064	1.44	0.18	0.9
100	196	0.0097	1.61	0.26	1.3
110	177	0.0138	1.83	0.37	1.8
120	154	0.0202	2.16	0.54	2.7
130	135	0.0272	2.53	0.72	3.6
140	130	0.0293	2.69	0.78	3.9

Hackney Technical Institute, London,
December, 1909

THE THERMODYNAMICS OF COMPRESSIBILITY AND EXPANSION

BY PHILIP BLACKMAN

PART I

SEC. 1. Let any substance, whether an element or a compound, and whether a solid, liquid, or gas, have a coefficient of cubical expansion at temperature t_1° C equal to c. Let also, at the same temperature, e represent the coefficient of compressibility of that substance. Then the pressure (atmospheres) required to compress isothermally at t_1° unit volume of the substance by the amount c is clearly equal to c/e, and the work done to produce this result is

$$\frac{76 \times d \times 981 \times c}{e} \text{ ergs}$$

(where d = the specific gravity of mercury at t_1° C).

SEC. 2. Let the body, which is now under the compressing force of c/e atmospheres, be heated, at constant pressure, till it recovers unit volume. If s_p be the specific heat at constant pressure, g its specific gravity, and t_2° C the final temperature, the heat absorbed is

$$s_p . g(t_2 - t_1).$$

SEC. 3. Let the substance, under the compressing force of c/e atmospheres and at the temperature t_1° C, be cooled, at constant volume, until the pressure falls to its original (initial) value. If s_v be the specific heat at constant volume and t_2° C the final temperature, the heat abstracted is

$$s_v . g(t_1 - t_2).$$

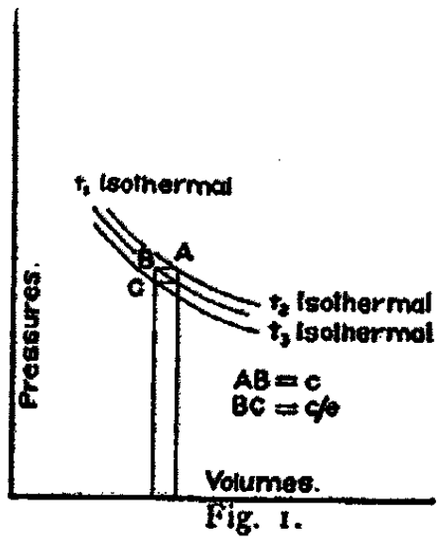

Fig. 1.

SEC. 4. If a PV-thermodynamic-diagram, Fig. 1, be drawn to illustrate the above three processes, the area representing the work done in Section 1 is very approximately equal to the mean of the areas representing the heat energies in Section 2 and Section 3, that is, equal to

$$\tfrac{1}{2}\, g\{s_p(t_2 - t_1) + s_v(t_1 - t_3)\}.$$

By the "First Law of Thermodynamics" we have

$$\frac{\text{the work done}}{\text{the heat expended}} = \frac{76 \times d \times 981 \times c}{\tfrac{1}{2}\, eg\{s_p(t_2 - t_1) + s_v(t_2 - t_1)\}}$$

$$= J \text{ (Joule's equivalent)}$$

$$= \text{constant};$$

whence

$$\frac{c}{eg\{s_p(t_2 - t_1) + s_v(t_1 - t_3)\}}$$

$$= J/76 \times d \times 981 \times z$$

$$= \text{constant.}$$

For the sake of simplicity put

$$z = s_p(t_2 - t_1) + s_v(t_1 - t_3),$$

then

$$c/egz = \text{constant.}$$

SEC. 5. In the case of solids and liquids s_p and s_v are equal so that on simplification

$$z = s(t_2 - t_3),$$

where s is the specific heat as ordinarily understood.

SEC. 6. It can be very easily shown that

$$t_2 - t_1 = 1^\circ \text{C}$$

and

$$t_1 - t_3 = 1^\circ \text{C}.$$

(1) Imagine a substance, of unit volume compressed isothermally to volume $1 - c$ under a compressing force of c/e atmospheres; now heat it 1° C, and its volume at $(t_1 + 1)^\circ$C becomes $1 - c + c = 1$ = initial (original) volume; but $(t_1 + 1^\circ)\text{C} = t_2$,
therefore

$$t_2 - t_1 = 1^\circ \text{C}.$$

(2) Consider the body at temperature t_1° C, volume $1 - c$, and under a compressing force equal to c/e atmospheres. Now to reduce the initial (= 1) volume by the amount c (to $1 - c$) and maintain it thus requires the force

c/e. But if the volume is maintained at $1 - c$ by some other means the force to do this becomes unnecessary or c/e may be put equal to O. To effect this let the substance be cooled 1° C, *i. e.*, to $(t - 1)$° C, which of itself would tend to reduce the volume from 1 to $1 - c$; hence $(t_1 - 1)$° C $= t_3$, or

$$t_1 - t_3 = 1° \text{ C}.$$

Therefore the expression

$$z = s_p(t_2 - t_1) + s_v(t_1 - t_3)$$

simplifies to

$$z = s_p + s_v \text{ (for gases)},$$

and

$$z = 2s \text{ (for solids and liquids)}.$$

SEC. 7. In the cases of gases the coefficient e is obtainable very simply by physical determination, but for solids and liquids this is a matter of very great difficulty.

The formula

$$c/egz = \text{constant}$$

may, with the above limitations for solids and liquids, be written

$$c/eg2s = \text{constant},$$

or

$$c/egs = \text{constant}.$$

If we designate a number of bodies by the symbols a, β, etc., and the corresponding quantities for the coefficients of cubical expansion, coefficients of compressibility, specific gravities, and specific heats by the symbols c_α, c_β, etc., e_α, e_β, etc., g_α, g_β, etc., and s_α, s_β, etc., respectively, we have

$$\frac{c_\alpha}{e_\alpha g_\alpha s_\alpha} = \frac{c_\beta}{e_\beta g_\beta s_\beta} = \ldots\ldots\ldots;$$

whence

$$e_\alpha = \frac{e_\beta c_\alpha g_\beta s_\beta}{c_\beta g_\alpha s_\alpha},$$

a result which admits of the comparison of the coefficients of compressibility of all solids and liquids.

London

NEW BOOKS

High-Speed Steel. *By O. M. Becker. 24 × 17 cm; pp. v + 360 pp. New York: McGraw-Hill Book Co., 1910. Price, $4.00.*—The subject is treated under the following heads: The development and nature of high-speed steels; making the steels and tools; the tool at work; the new requirements; problems involved in the use of the high-speed steels; appendices.

The author says, page 38, that "the indications, at present, are that austenite is a solid solution of carbon in gamma iron, that martensite is a solid solution of carbon in beta iron, and that troostite is a solid solution of carbon in alpha iron. Theoretically neither beta nor alpha iron can be maintained in solid solution with carbon, and therefore austenite is the only stable one of these solutions, and martensite and troostite must be considered as instable constituents and merely transition stages between austenite and pearlite. In other words, when the solution of gamma iron falls to the temperature at which it breaks up, it changes to the solution of beta iron; this being an abnormal solution at once breaks down into the solution of alpha iron (provided, of course, that it is not obstructed), and the alpha solution being also abnormal breaks down into pearlite, which is not a solution at all but a mere mixture of crystals of ferrite and cementite so fine in structure that the high powers of the microscope are necessary to show its structure."

The author's explanation of the hardening of steel, page 32, is as follows:

"If any carbon steel be heated to a high enough temperature, it will be entirely converted into austenite. If now the steel in this condition be cooled with great rapidity, we may bring it to the atmospheric temperature with a part of its molecules still left in the austenitic condition; and since the austenitic molecule is much harder than the pearlitic molecule [?], it is on this principle that the hardening of steel by sudden cooling is explained. No cooling has ever been so rapid, however, as to obtain all the molecules in the austenitic condition, because, although the change from austenite to pearlite is a tardy one, it is not so slow that we can get away from it all together.

"There are some conditions, however, which aid in keeping some of the steel in the austenitic condition. One of these is the influence of carbon, which tends to obstruct the change and make it more tardy. Thus with 1.60 percent carbon in steel, and with very rapid cooling, we may find under the microscope as much as 70 percent of the mass in the austenitic condition, but this is about the maximum that has been obtained up to this time by quick cooling and carbon content only.

"Again, the importance of carbon in this respect is shown by the observation that, unless some carbon is present, we cannot retain any of the steel in the austenitic condition, no matter how rapid the cooling or what other elements—tungsten, manganese, chromium, etc.—be present. We may cool it with such extreme rapidity that it is brought to the temperature of the atmosphere in the austenitic condition, but with no more than traces of carbon present it gradually changes over, even when cold, to the pearlite condition. We may express this by saying that we can catch, or trap, the austenite in the steel by means of quick cooling, but we cannot "fix" any of it there except with an influential

proportion of carbon. The tendency of austenite to revert to the normal, or pearlitic, condition at all temperatures below 700° C is so strong that it will do so even when cold unless carbon is present as a fixing agent. The colder the steel, the more slowly the reversion proceeds, however."

In the self-hardening steels the inversion normally occurring about 735° C takes place below ordinary temperatures. This would seem to make self-hardening steels ideal; but the hypothesis of the martensite stage saves the author, page 39, from this conclusion. "As has been shown, the change from austenite to martensite is a very quick one, and difficult to prevent. Thus even manganese steel, if allowed to cool slowly in the mold into which it is poured, will be wholly or partly in the martensitic stage at atmospheric temperatures. In this condition it is not only very hard, but also very brittle. By heating it to a white heat (over 1000° C) and cooling very rapidly, as by plunging it into ice water, we can, however, entirely fix the austenitic stage in this steel. This fixation of the austenitic stage makes the steel not so hard as it was when in the martensitic condition, but still very much harder than in the pearlitic. It is also very tough; but unfortunately it has such a low elastic limit that the thin edge of a tool will not stand up under the shocks of service, but crumbles away, so that manganese steel is not suitable for making cutting tools.

"The effect of nickel on hardening is the same in kind as that of manganese, but it takes about twice as much nickel to produce this effect. As ordinary nickel steel contains usually only about 3.5 percent of nickel, and as it requires about 25 percent to bring the temperature of the change below that of the atmosphere, commercial nickel steel is not a self-hardening steel, but is used for other purposes."

"Tungsten acts first as a strong obstruction to all the steps in the change from austenite to pearlite, so that when we have 7 percent or more of tungsten present, a moderately rapid cooling, even such as allowing the bar to cool in the air, will prevent the change to pearlite. Indeed, when tungsten steels are to be annealed and the pearlite stage produced, it is necessary that the cooling shall be very slow indeed, occupying several times as long as the annealing of normal carbon steels.

"Tungsten acts secondly as a powerful fixing agent for martensite. It has been already shown that martensite is not stable in normal carbon steel even after it has been induced there by hardening, unless the metal be kept cool. Warming it up to the so-called temper heats changes the martensite over to troostite, and if the heating be continued, even the effective hardness of troostite is lost long before the steel reaches a red heat. The presence of 7 percent or more of tungsten, however, increases the stability of martensite so much that the steel may be heated well above the tempering heats before the martensite even begins to break down into troostite or pearlite."

"It is now possible to explain the theory of the effect produced by the special heat treatment applied to high-speed tools. The first treatment, that is, a moderately rapid cooling from a very high temperature, is sufficient to retain the steel chiefly in the austenitic condition by virtue of the tungsten present. The second or low-heat treatment then changes the austenite partly or wholly into martensite, thus further increasing the cutting efficiency of the

tool by increasing the hardness. Subsequently the tungsten present acts by preserving the martensite even when the steel is heated up nearly to a red heat by the friction of the work.

"If we ask why it is necessary first to cool the steel from so high a temperature as to obtain the austenitic structure, and then to let down this austenitic structure to martensite by reheating, instead of cooling for martensite in the first instance, it is to be observed that, unless the cooling begins at a very high heat, austenite is changed in part to troostite, and then the tungsten present is not sufficient to prevent the softening proceeding still further when the steel is heated up by the friction of rapid work. In short, if we allow the change to proceed beyond a certain point, it is difficult to check it hereafter."

This is a bit vague. One can hardly accept the pearlitic molecule and there is a good deal of playing fast and loose with the stability of the hypothetical martensite. It is quite clear that the theoretical side of the matter is pretty uncertain. This however is not the fault of the author who is writing primarily as an engineer. The practical side of the book is very good indeed, and there is much in it of interest. The reviewer was glad to note the strong stand taken, page 155, in regard to the unreliability of the eye as a temperature gauge. It would have been well, however, if the author had pointed out that the optical pyrometers, as calibrated, do not give accurate readings if sighted on molten metal and especially not if sighted on a stream of molten metal.

Wilder D. Bancroft

Hypochlorite und elektrische Bleiche. *By Willy Ebert and Josef Nussbaum. 18 × 25 cm; pp. xii + 356. Halle: Wilhelm Knapp, 1910. Price: 18 marks.*—The authors treat their subject under the following heads: general information in regard to electrochemical preparation of bleach; technical apparatus; the running of a plant; electrolytic bleach. The authors begin with the general theory; then they take up the various types of electrolyzers. There are short chapters on how to make and maintain the salt solutions; on how to start the plant and on how to keep it going. The last chapter deals with the product: analysis; permanency; uses; methods of bleaching; costs; comparison between electrolytic bleach and bleaching powder.

The authors distinguish three types of electrolyzers: those with platinum electrodes only (Kellner); those with platinum anodes and graphite cathodes (Schoop, Schuckert); those with graphite electrodes only (Haas and Oettel). The improved form of the Kellner apparatus, page 117, now has horizontal gauze electrodes and the solution circulates horizontally through the cells instead of vertically. The authors naturally do not believe that the Oettel type of machine is as good as the Kellner type and they are a good deal grieved, page 169, that Haas and Oettel should, in the beginning, have shown themselves much cleverer at advertizing than Siemens and Halske.

Under the general headings of uses of bleach the authors give an admirable sketch of cellulose and its properties in their bearing on the process of bleaching. Take it all in all, this is distinctly one of the successful books of the series.

Wilder D. Bancroft

Die Metallurgie des Zinns, *mit spezieller Berücksichtigung der Elektrometallurgie. By Hans Mennicke. 18 × 26 cm; pp. viii + 196. Halle: Wilhelm*

Knapp, 1910. Price: 10 marks.—The author gives a great deal of information and seems to have covered the ground pretty thoroughly. The chief fault of the book is that one gets the impression that nearly all the improvements worth making have been worked out by the author. Of course this may be true; but the reviewer feels a bit sceptical. *Wilder D. Bancroft*

The Chemistry and Testing of Cement. *By Cecil H. Desch. 15 × 22 cm; pp. xi + 267. New York: Longmans, Green & Co., 1911. Price: $3.00.*—The subject is treated under the following headings: the history of calcareous cements; the raw materials and processes of manufacture of cements; the constitution of cements; the setting and hardening of cements; the physical properties of cements; the mechanical properties of cement, concrete and artificial stone; the resistance of cement and concrete to destructive agents; the chemical analysis of cements; conclusion.

The author has treated the subject from the point of view of the chemist. The discussion of the setting of mortar is based on the theory of Michaelis, that the principal products of the reaction are not crystalline but colloidal. Reference is made to the work of Shepherd, Wright and Rankin on the nature of the phases and the book seems to be distinctly a good one.

The paragraphs on the Roman mortar, page 3, and on the hardening of lime mortar, page 110, are of such general interest that I quote them.

"Whether the Egyptians were acquainted with the use of lime or not, the Greeks must have adopted this material at an early period, and the Romans must have borrowed it from them. The mortar was prepared in the modern fashion, by slaking the lime and mixing with sand, and the examples of Roman brickwork which still exist are sufficient evidence of the perfection which the art obtained in the ancient times. The remarkable hardness of the mortar in walls of Roman workmanship has sometimes led to the assumption that some secret was possessed by the workmen which is now lost, but a comparison of the analyses of the mortar with the descriptions of the method by ancient authors gives no ground for such a supposition. The good quality of the mortar is due simply to the thorough burning and fine grinding of the lime and the very thorough mixing of the slaked or "tempered" lime with the sand. We know that this, the essential operation of building with mortar, was not left to unskilled laborers, but was the special task of the master. The subsequent history of building abounds in examples of differences in the attention paid to this all-important point."

"The desiccation of a colloid is accompanied by considerable contraction of volume. Gelatinous silica, clay, or any other colloidal substance, if spread in a layer and dried, cracks into irregular fragments as the water disappears by evaporation, and similarly, a plastic mass of lime would shrink so much in drying that it would crack and lose its form. The shrinkage is lessened by mixing with an inert substance, such as sand, the particles of which become coated with lime, which adheres to them tenaciously. The cohesion of the dried colloid and its adhesion to the sand surfaces are the cause of the mechanical strength of mortar, which is able to resist not only the tensile stresses due to shrinkage, but also the external stresses to the mortar.

"A further reaction occurs when lime mortar is exposed to air for any length of time. Carbon dioxide is absorbed, and a part of the calcium hy-

droxide is converted into calcium carbonate. The presence of moisture is essential to this reaction, as dry carbon dioxide is without action on dry lime. The calcium carbonate thus formed is crystalline, and the crystals, formed by slow growth in a colloidal medium, are closely interlaced, and form a coherent mass. This subsequent reaction is not essential to the formation of a hard mortar, as is sometimes supposed. The only essential process is the desiccation of the colloid, and the hardening by conversion into carbonate is merely a secondary reaction. It is confined to the outer layers of a mass of mortar, and by the formation of an impervious coating, hinders the access of carbon dioxide to the interior. It is therefore not surprising that mortar taken from old Roman buildings, if uninjured, is found to consist mainly of calcium hydroxide, even 2000 years of exposure to the atmosphere having been insufficient to convert more than a superficial layer into carbonate."

Of importance for the theory of colloids is the fact, page 58, discovered by Michaelis, that if quartz is reduced to an impalpable powder by prolonged grinding, it becomes so active as to be converted into colloidal hydrated silicic acid by merely boiling with water. *Wilder D. Bancroft*

Physikalische Chemie der Zelle und der Gewebe. *By Rudolf Höber. 17 × 25 cm; pp. xv + 671. Leipzig: Wilhelm Engelmann, 1911. Price: 17.25 marks.* —The subject is treated under the following heads: osmotic pressure and theory of solutions; osmotic pressure in organisms; disssociation theory; equilibrium in solutions of electrolytes; quantitative determination of hydrogen and hydroxyl ions; osmotic properties of the cell, and the lipoid theory; criticism of the lipoid theory, and mechanism of physiological transference; surface phenomena; colloids; action of single electrolytes; action of mixed electrolytes; electrical processes at physiological membranes; ferments; physical chemistry of nutrition.

The book is a remarkably good one, the chapter on colloids, for instance, being a treatise in itself. Many of the other chapters are almost equally good and one can open the book anywhere with the certainty of finding something interesting before he has read more than a few pages.

In the preface to this edition the author says: "When revising the book I considered leaving out the pure physical chemistry and incorporating only what bore directly on the phenomena of life. I decided finally that it is safer to assume a knowledge of organic chemistry than a knowledge of the essential fundamentals of physical chemistry. I have therefore kept the original form of presentation. This has the advantage that it brings out clearly the fact that in future we must subdivide physiology and that the part treated in this book is as much a distinct field as is physiological chemistry." *Wilder D. Bancroft*

Contribution a l'histoire de la Chimie. *By A. Colson. 17 × 25 cm; 130 pp. Paris: A. Hermann et Fils, 1910. Price: 3 francs.*—The author thinks that Ladenburg's book ignores French work more than it should. He has therefore set himself the task of presenting matters in a more satisfactory way. There is no doubt but that we get a new perspective, and that it is always interesting. The author believes that Gerhardt's theory of types has been of more importance in the development of organic chemistry than the assumption of tetravalent carbon. Like a skilled disputant he asserts this boldly as a

matter not requiring proof. There are a good many things that the author has apparently not read, because he proposes to account for abnormal molecular weights in solution by assuming polymerization of the liquid solvent. These two points are characteristic of the book. *Wilder D. Bancroft*

Kometen und Elektronen. *By Augusto Righi. 15 × 22 cm; 64 pp. Leipzig: Akademische Verlagsgesellschaft, 1911. Price: 2.40 marks.*—The first chapter deals with the pressure of light, the second with the constitution of a comet's tail, and the third with the action of the pressure of light upon gases. Next we have a discussion of electrical phenomena in comets and lastly the question whether the earth passed through the tail of Halley's comet on May 19, 1910. The author thinks that it did.

The theory of Arrhenius is accepted, that cosmic dust forms the luminous matter of the comet's tail and that it is connected with the Northern Lights. In regard to the size of a comet's tail, the author says: "It is very probable that what we see of a comet's tail is only a small part of it. The luminous discharge, from which we believe that the light of the tail chiefly comes, must diminish gradually towards the actual edges of the tail and also at a distance from the body of the comet. Consequently the tail must cease to be visible at the points where the particles of dust and the gas molecules become few and far between; but while there are still some there. A consequence of this is that the earth might pass through the periphery of a comet's tail when direct observations would lead one to believe that the earth was still at some distance from the tail." *Wilder D. Bancroft*

Introduction a la Métallographie microscopique. *By P. Goerens. Translated and revised by A. Corvisy and F. Robin. 17 × 26 cm; 227 pp. Paris: A. Hermann et Fils, 1911. Price: 10 francs.*—The subject is treated under five heads: physical properties of matter; microscopic study of metals; physical mixtures; alloys; metallography of the carbon steels. The book is a good one though it is not by any means up-to-date. An excellent feature of the book is that a large number of diagrams are given. *Wilder D. Bancroft*

Radiumnormalmasse *und deren Verwendung bei radioaktiven Messungen. By E. Rutherford. 15 × 22 cm; 45 pp. Leipzig: Akademische Verlagsgesellschaft, 1911. Price: 1.50 marks.*—At the congress of Radioactivity held in Brussels last year, it was voted that a standard of radioactivity be prepared by Mme. Curie which should be official the world over. The amount of emanation in equilibrium with one gram of radium is to be known as a "Curie." In this pamphlet the author points out the importance of having a standard of radioactivity, shows how one would be established and discusses the permanency of it. *Wilder D. Bancroft*

Die Zustandsgleichung. *By J. D. van der Waals. 15 × 22 cm; 24 pp. Leipzig: Akademische Verlagsgesellschaft, 1911. Price: 1.50 marks.*—This is the address delivered on receiving the Nobel prize. The author sketches the development of his well-known equation of state. Very interesting is the statement that apparently no equation of state is possible unless one postulates an association of molecules to larger complexes. *Wilder D. Bancroft*

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