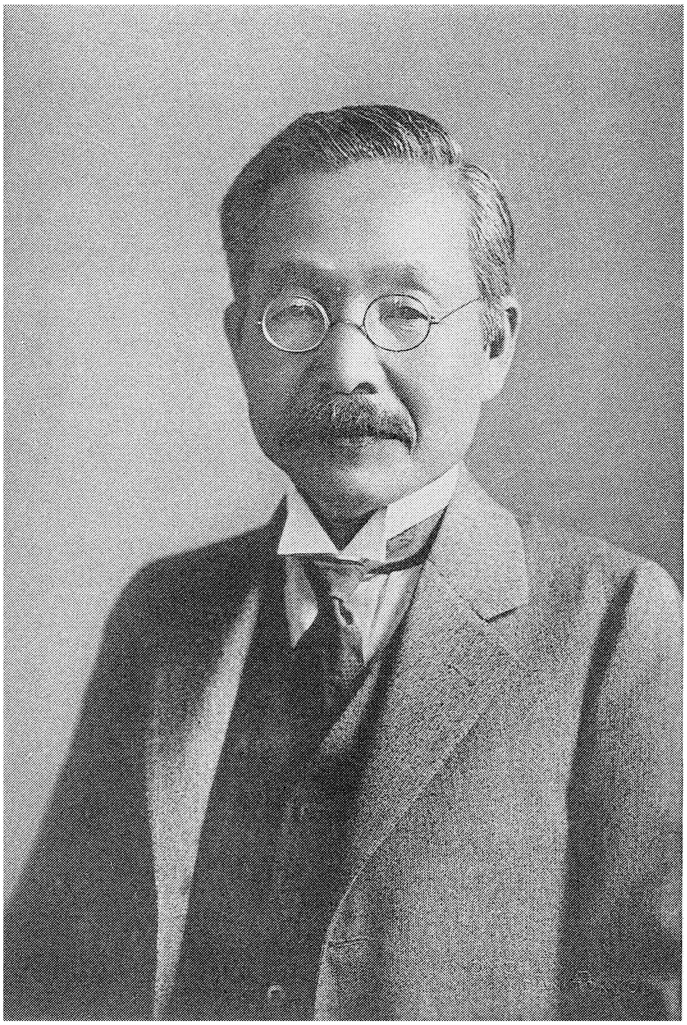

PROFESSOR KIKUNAE IKEDA.

Kikunae Ikeda was born in Kyoto on October 8th., 1864, as the second son of Harunae Ikeda. His family belonged to the Satsuma Clan, which was one of the most outstanding in introducing western learning in Japan and played most conspicuous role at the time of the Meiji Restoration.

After learning English and eastern classics at several places, young Ikeda entered the preliminary course of the Tokyo University in 1882. Soon he distinguished himself as a most promising student, and graduated the course of chemistry in the College of Science of the University in 1889.

During six years, from 1890 to 1896, he taught in the Higher Normal School. His efforts in improving chemical education in Japan, by introducing rising principles of physical chemistry as the basis, has been widely acknowledged.

In 1896 he was called back to his *alma mater* as an assistant professor in the College of Science, and three years later was sent abroad as a government research fellow. From 1899 to 1901 he studied in the Laboratory of Prof. Ostwald in Leipzig, where many young physical chemists crowded from all parts of the world at that time. After staying for a few months in the Davy-Faraday Research Laboratory of the Royal Institution, London, he returned home and was promoted to the professor of physical chemistry in the Tokyo Imperial University. Soon he took the degree of Rigakuhakushi and directed the chemical institute from 1912 until he retired from the chair on March 1923.

Professor Ikeda was elected a member of the Imperial Academy of Tokyo in 1919. On the establishment of the National Research Council of Japan in 1920, he was elected one of the members, and served as the vice-chairman of its Division of Chemistry from 1921 to 1923. The title of Honorary Professor of the Tokyo Imperial University was bestowed to him on his retirement from the active service in the University. Since the Institute of Physical and Chemical Research was established in 1916, he directed its chemical department until 1921, and still remains there as an active member of the Institute.

Professor Ikeda's works as a physical chemist are chiefly in the field of chemical kinetics and the theory of solutions. As early as 1894 he published a paper on velocity of oxidation of phosphorus. His work with Bredig on the catalytic action of colloidal platinum is well known. He tried an extension of the theory of ideal solution from chemical standpoint, the result of which was published in 1908. Many works on chemical kinetics, enzyme actions and vapour tensions of solutions have been published chiefly in the name of his pupils.

Besides physical chemistry, Professor Ikeda has very wide and keen interest in almost every part of chemistry. Especially his success in the practical application of chemistry ought not be passed without notice. He discovered the importance of the salts of glutamic acid and other decomposition products of proteids as the principles of taste in food. "Ajinomoto," verbally taste essence, which is the name given to the product manufactured according to his patent method, is very popular in Japan, being used in household cookings. He applied properly dehydrated acid clay as the adsorbent of moisture. The preparation under the name "Adsole" is now getting great reputation for adjusting humidity in public buildings.

In order to celebrate the sixtieth anniversary of the birthday of Professor Ikeda which was due October last year, his many friends and former pupils have raised a considerable sum of money, which was presented, according to the wish of Professor Ikeda, to the Chemical Society of Japan as a fund for promoting scientific publications. The Society gratefully decided to undertake the publication of short papers or abstracts in European languages, which took the form of this Bulletin.

November, 1925.

Masao KATAYAMA.

A SIMPLE DERIVATION OF PLANCK-EINSTEIN'S FORMULA.

By **Masao KATAYAMA.**

Received November 13, 1925. Published January 28, 1926.

A monatomic solid containing n atoms is considered. It is assumed that each atom oscillates with a fixed frequency ν, its energy being distributed equally for each of three degrees of freedom of atomic motion, and that the energy exchanges for one degree of freedom take place only in integral multiples of a quantum $h\nu$, where h denotes a universal constant. The difference between atoms having different quanta of energy can be regarded, from the standpoint of energetics, similar to the difference of isomeric molecules. The equilibrium between these atoms can be treated in the same way as a chemical equilibrium between isomers.

The energy of each kind of atom in the solid is uniquely determined by ν, and therefore the energy of a system composed of several kinds of atoms is equal to the sum of energy of each kind taken separately. The volume of each atom is constant at a given temperature, and therefore the total volume is also additive. Now a homogeneous mixture in which the energy and volume are additive is known as an ideal solution, the dilute solution being its special case. A chemical equilibrium in such a system follows the law of dilute solutions, and the equilibrium constant can be calculated in the ordinary way.

Let molar fractions of atoms whose energy for one degree of freedom is equal to 0, $h\nu$, $2h\nu$, $3h\nu$,…… $mh\nu$…… be respectively n_0/n, n_1/n, n_2/n, n_3/n…… ……n_m/n…… The equilibrium constant of the transformation of atoms having energy zero to those having energy $mh\nu$ is n_m/n_0. The energy absorbed in the change is $mh\nu N$ for one gram atom, N being Avogadro's constant. Then we have for a small change of absolute temperature T,

$$\frac{d\, ln\frac{n_m}{n_0}}{d\,T}=\frac{mh\nu N}{RT^2}, \qquad \text{R : Gas constant.}$$

Since ν is assumed to be constant independent of temperature, the following relation is obtained by integration.

$$ln\frac{n_m}{n_0}=-\frac{mh\nu N}{RT}+C.$$

The integration constant C can be easily known to be zero. For in the limiting case $m=0$, we have

$$n_m = n_0,\quad mh\nu = 0,\qquad \text{so}\quad C=0.$$

Then the result of integration can be transformed to the following form.

$$\frac{n_m}{n_0} = e^{-\frac{mh\nu}{kT}},$$

k denoting Boltzmann's constant which is equal to R/N.

The number of each kind of atoms, n_0, n_1, n_2, $n_3 \cdots\cdots$ $n_m \cdots\cdots$, can now be expressed as follows:

$$n_0,\ n_0 e^{-\frac{h\nu}{kT}},\quad n_0 e^{-\frac{2h\nu}{kT}},\quad n_0 e^{-\frac{3h\nu}{kT}},\quad \cdots\cdots n_0 e^{-\frac{mh\nu}{kT}},\ \cdots\cdots$$

The total number n is equal to the sum of these values:

$$n = n_0\left(1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + e^{-\frac{3h\nu}{kT}} \cdots\cdots\right) = n_0 \frac{1}{1 - e^{-\frac{h\nu}{kT}}}.$$

Now the total energy E for all three degrees of freedom is equal to

$$3(0 + h\nu n_1 + 2h\nu n_2 + 3h\nu n_3 + \cdots\cdots),$$

i.e.

$$E = 3h\nu n_0 e^{-\frac{h\nu}{kT}}\left(1 + 2e^{-\frac{h\nu}{kT}} + 3e^{-\frac{2h\nu}{kT}} + \cdots\cdots\right).$$

If the mean energy of an atom be denoted with ε, we have

$$E = \varepsilon n = \varepsilon n_0\left(1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \cdots\cdots\right).$$

The series in bracket in the former equation for E is evidently equal to the square of that in the latter equation. We have thus by equating these two equations,

$$3h\nu e^{-\frac{h\nu}{kT}}\left(1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \cdots\cdots\right) = \varepsilon,$$

i.e.

$$\varepsilon = 3h\nu \frac{e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}} = 3\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

This is the equation of Planck-Einstein for the mean energy of an atom in a monatomic solid.

In the transformation of one gram atom of a certain kind of atom having energy $mh\nu$ to another kind having $m'h\nu$, in the same concentration, the maximum work or the decrease of free energy is equal to $RTln\frac{n_{m'}}{n_m}$, while the increase of energy is $(m'-m)h\nu N$. Now it is easily seen from the above results that

$$ln\frac{n_{m'}}{n_m} = -\frac{(m'-m)h\nu}{kT} = -\frac{(m'-m)h\nu N}{RT}.$$

This shows that the change of free energy and total energy is always equal to each other for such transformations. The theory of the action quantum, *i.e.* of the energy quantum proportional to frequency, is equivalent to the assumption that the equilibrium of interatomic exchange of energy in a solid can be treated as a chemical equilibrium and Berthelot-Thomsen's principle can be applied to this equilibrium.

Chemical Institute, Faculty of Science, Tokyo Imperial University.

ON THE RATE OF FLOW OF VARIOUS GASES THROUGH A POROUS WALL.(1)

By Jitsusaburo SAMESHIMA.

Received October 27, 1925. Published January 28, 1926.

The velocity of effusion of various gases through a perforated thin plate is expressed by the well known equation $t=k\sqrt{M}$, where t is the time of effusion of the definite volume of gas whose molecular weight is M, and k is a constant. This formula was derived by Schmidt(2) and then verified by Graham,(3) Ramsay and Collie(4) and Donnan.(5) If we use, however, a porous wall such as an unglazed earthenware of compact quality, the above equation can no more be applied as is to be seen from the following experiment.

The apparatus used is shown in Fig. 1. A is a small circular disc of compact unglazed earthenware, the diameter of which is 0.6 cm. and the thickness is 0.15 cm. The disc is attached to an end of a glass tube with sealing wax. The glass tube is connected to a vacuum pump and the pressure is always kept lower than 0.1 mm. The disc is kept at 25° by circulating the water of a thermostat as shown in the figure. The bulb B has a capacity of about 70 c.c. and marked at its upper and lower necks $-C$ and $D-$ with lines. A platinum wire attached at the point E on the side-tube serves as the indicator of the constancy of the gas pressure. The gas is put into the vessel B and then the cock F is opened. Now the gas escapes through A and the mercury head goes up. The time which the mercury head requires to pass from D to C is observed. The pressure indicated on the scale H is kept constant during an experiment by raising gradually the mercury reservoir G. The temperature is always kept at 25.°00.

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(1) Read before the Chemical Society of Japan, April 4, 1925.

(2) Schmidt, *Gilb. Ann.*, 66 (1820), 39.

(3) Graham, *Phil. Trans.*, 55 (1846), 573.

(4) Ramsay and Collie, *Proc. Roy. Soc.*, 60 (1897), 206.

(5) Donnan, *Phil. Mag.*, [5] 49 (1900), 423.

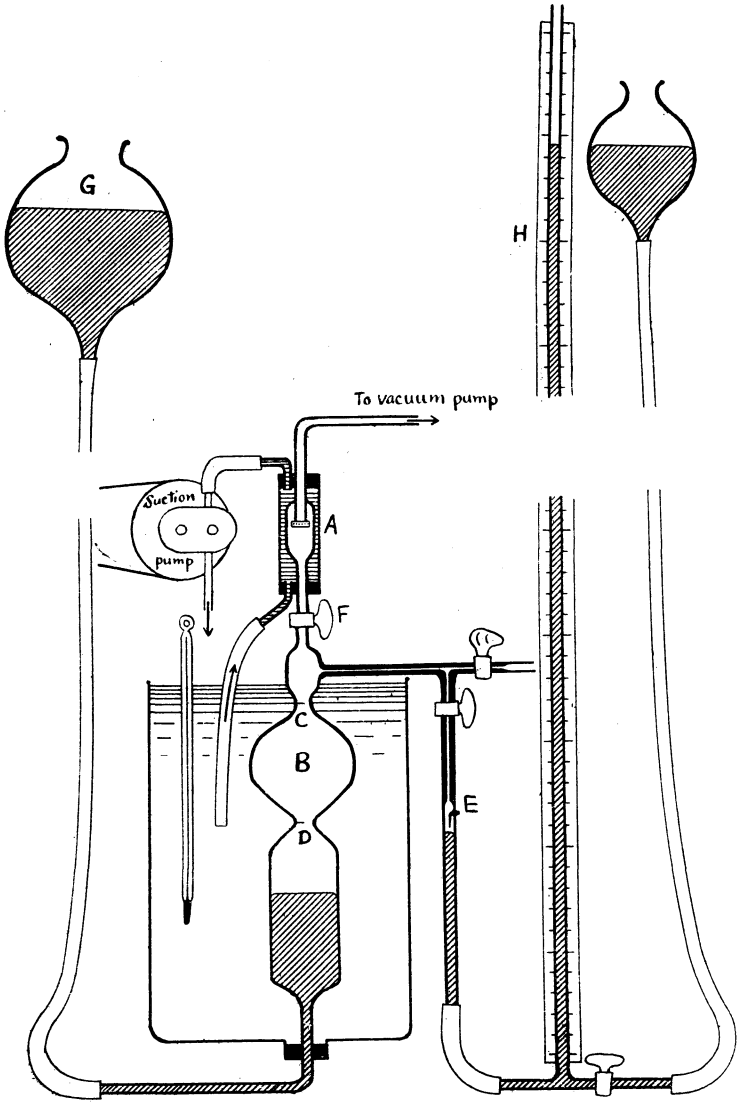

Fig. 1.

The gases examined were methane, ammonia, acetylene, ethylene, air, oxygen and carbon dioxide. All gases except air and oxygen were purified by washing with appropriate reagents and then fractionated by using the liquid air. Oxygen was made from potassium permanganate and passed through the tubes of calcium chloride, potassium hydroxide and phosphorus pentoxide. The results are shown in the following table. Moreover, the time of flow through a perforated platinum plate under one atmospheric pressure has been measured, and the results are also shown in the same table.

Gas.	Time of effusion through an unglazed earthenware, in seconds.				Time of effusion through a perforated Pt. plate.	Mol. weight of gas.
	1.0 atm.	1.5 atm.	2.0 atm.	2.5 atm.		
Methane	962	785	664	573	176.2	16.037
Ammonia	944	762	637	548	178.4	17.032
Acetylene	1048	830	685	583	216.0	26.026
Ethylene	1080	849	700	599	225.7	28.042
Air	1414	1169	1003	878	230.9	28.96
Oxygen	1521	1268	1090	956	243.4	32.000
Carbon dioxide	1457	1162	968	829	279.4	44.005

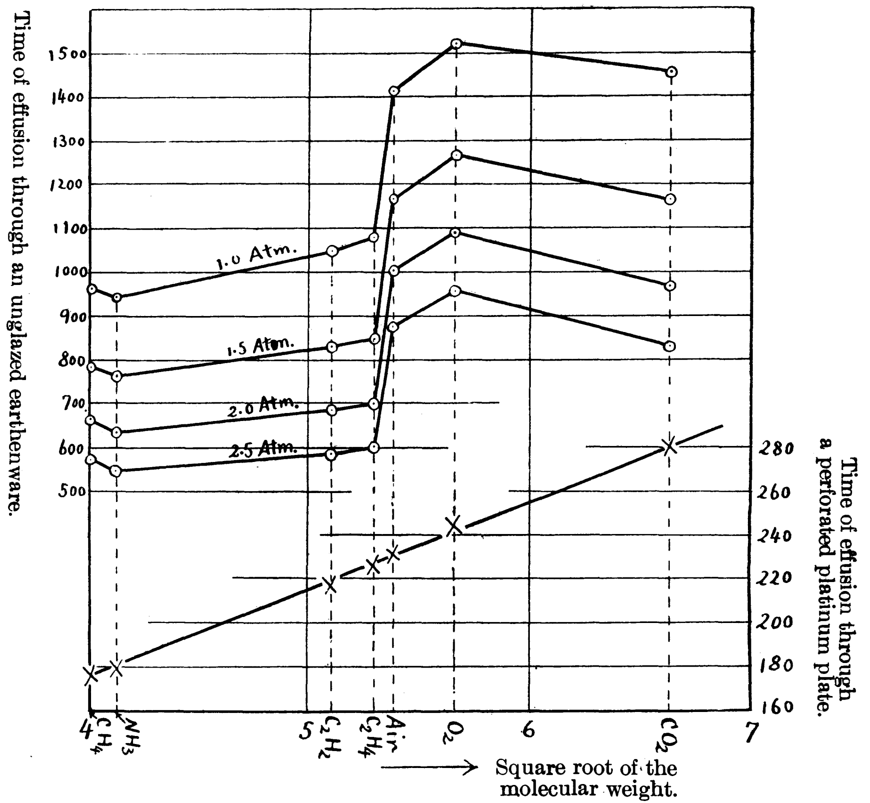

Fig. 2.

In Fig. 2 the square root of the molecular weight of gas is taken as abscissa and the time of effusion as ordinate. The circlets show the times of effusion through an earthenware under the pressures of 1.0, 1.5, 2.0 and 2.5

atmospheres, and the values corresponding to the same pressure are connected by straight lines. The results are far from expressed by the equation $t=k\sqrt{M}$. The crosses show the time of effusion through a perforated platinum plate. They lie nearly on a straight line, which means that they can be expressed by the above equation.

The time of effusion through an unglazed earthenware t will be expressed by the following equation,

$$t=k\eta^{n}M^{\frac{1-n}{2}}$$

where η is the viscosity coefficient of the gas, M is the molecular weight and k and n $(n<1)$ are two constants independent of the kind of gas but depend on the nature of the porous wall and the pressure of gas. If the wall be very thin then n approaches to zero and the equation takes the usual form $t=k\sqrt{\mathrm{M}}$, while if the wall be very thick (or a long capillary tube) then n tends to one and the equation becomes $t=k\eta$.

In the present experiment I have calculated the times of effusion from the above equation and the results are given in the following table. The values of the viscosity coefficients at 25° have been obtained by interpolations from the observed values of numerous authors at various temperatures.

Gas.	Viscosity coeff. at 25°.	Time of effusion calculated from the above equation.			
		1.0 atm. $k=24100$ $n=0.44$	1.5 atm. $k=50400$ $n=0.53$	2.0 atm. $k=79800$ $n=0.59$	2.5 atm. $k=104600$ $n=0.63$
Methane	1118×10^{-7}	957	779	657	566
Ammonia	1042 ”	943	761	638	548
Acetylene	1030 ”	1057	835	691	588
Ethylene	1015 ”	1072	844	696	592
Air	1850 ”	1409	1168	998	868
Oxygen	2080 ”	1525	1273	1092	951
Carbon dioxide	1550 ”	1465	1174	980	838

The differences between the observed (former table) and the calculated values (latter table) are within one percent excepting only a few cases.

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ON THE ABSORPTION SPECTRA OF SALT SOLUTIONS OF SOME RARE EARTH ELEMENTS.(1)

By Toshi INOUE.

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It is the well known fact that some salts of rare earth elements yield highly characteristic absorption spectra, by means of which, therefore, they are very conveniently detected. Concering to this subject we have indeed plenty of literatures to be referred;(2) notwithstanding I repeated the study of the absorption spectra of some rare earth salts, in order to know whether their spectra are influenced from each other by mixing them and further to investigate the absorptions in the ultraviolet region, which are wanting in the preceding studies.

Experimental.

1) Absorption Spectra of Chlorides of Lanthanum, Cerium, Praseodymium, Neodymium, Samarium and Erbium in the Visible Region.

Lanthanum chloride, being colourless, shows no absorption band in the visible part. Cerous chloride also shows no bands, but its end absorptions are extended to the region of the spectrum of comparatively long wave lengths: namely 10 cm. layer of its 0.05 mol aqueous solution absorbs even to 4200 Å (violet), and 0.2 mol solution (the same thickness of layer) absorbs to 4600 Å (blue violet). The aqueous solutions of praseodymium chloride, neodymium chloride, samarium chloride and erbium chloride absorb remarkably in visible part and they show very characteristic bands, which accord very well with the results attained by the works already published.

Brauner and others(3) have studied the mutual influences of the absorption spectra of the solutions of rare earth salts, when they were mixed with each other. According to them, the spectra change distinctly their appearances by contamination of other salts. But in my present investigation, this was by no means the case; I studied, with the special care, the absorption bands 4441 Å of praseodymium, 5222, 5205, 5123 and 5091 Å of neodymium and 4071 and 4013 Å of samarium in mixing the salt solutions to each other or adding lanthanum chloride to each solution. These characteristic bands, however, remained always unchanged, and it was thus accertained that these elements may at least be detected by means of these absorption bands. (Fig. 1).

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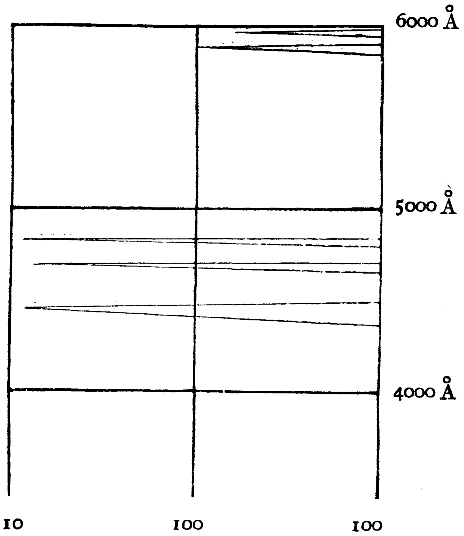
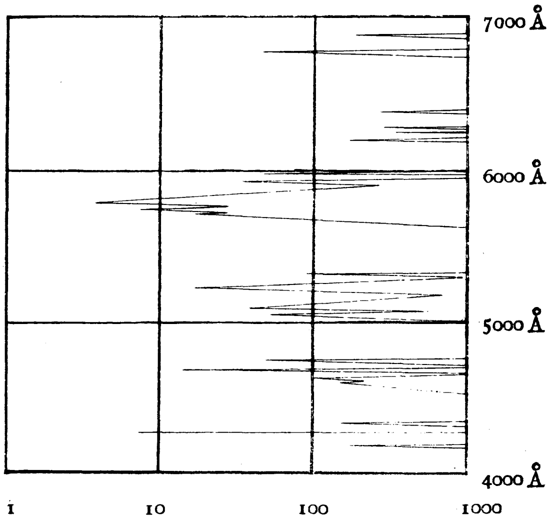
(1) Read before the Chemical Society of Japan, April 8, 1923.

(2) Compare "A Text Book of Inorganic Chemistry" by N. Friends, Vol. IV, p. 283, (1917).
W. Prandtl, *Z. anorg. Chem.*, 116 (1921), 96.
Z. F. Yntema, *J. Am. Chem. Soc.*, 45 (1923), 907.

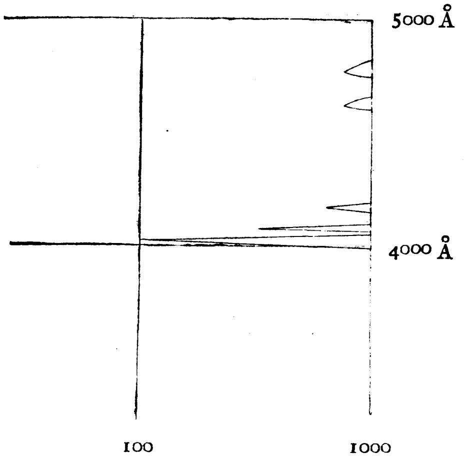
(3) B. Brauner, *J. Chem. Soc.*, 43 (1883), 278.
E. Demarçay, *Compt. rend.*, 126 (1898), 1039.



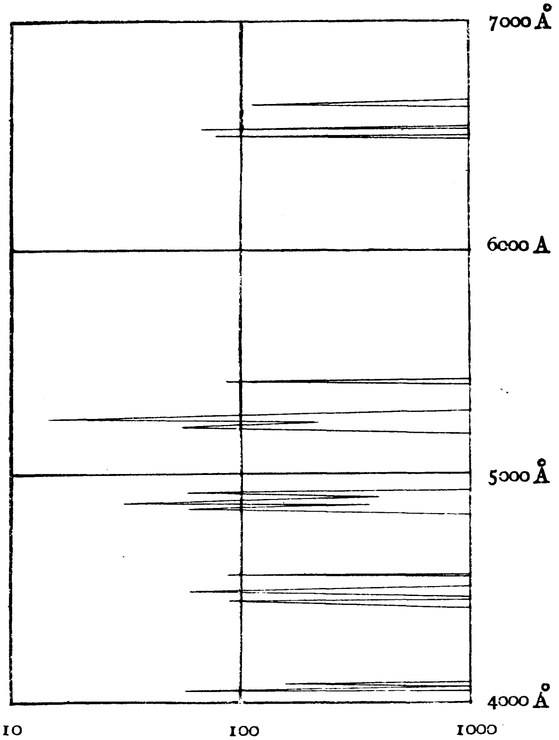
Relative thickness in mm. of
0.0256 mol solution
Praseodymium chloride.



Relative thickness in mm.
of 0.06 mol solution
Neodymium chloride.



Relative thickness in mm.
of 0.011 mol solution
Samarium chloride.



Relative thickness in mm.
of 0.02 mol solution
Erbium chloride.

Fig. 1.

2) Absorption Spectra in the Ultra-Violet Region.

Among chlorides of six rare earth elements above mentioned, only three, namely cerous chloride, samarium chloride and erbium chloride, show absorption bands in the ultra-violet region. As it will be seen in Fig. 2, cerous chloride possesses two bands, while both of samarium chloride and erbium chloride show only one in ultra-violet. The positions of their absorption maxima are given in the following table:

	Concentration in mol.	Thickness of liquid layer (cm.)	$\lambda(\text{Å})$	ν
$CeCl_3$	0.01 0.001	2.8 4.8	3350 2469	2985 4050
$SmCl_3$	0.11	1.4	2600	3850
$ErCl_3$	0.2	5.6	2470	4050

Chlorides of praseodymium, neodymium and lanthanum absorb only continuously in ultra-violet (compare Fig. 2.)

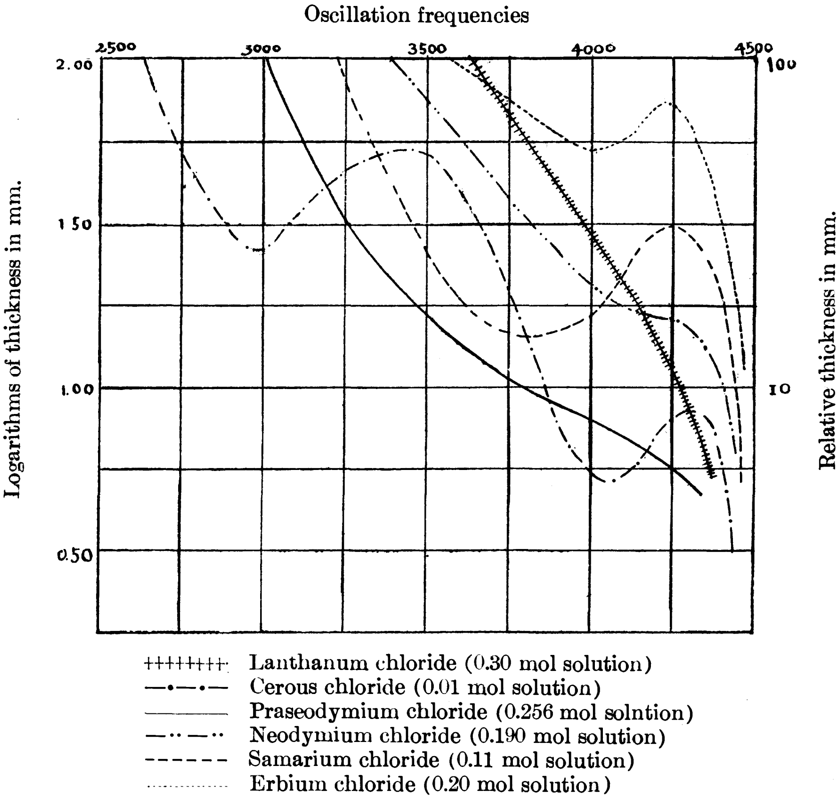


Fig. 2.

3) Application of Absorption Spectra for the Quantitative Determination of Some Rare Earth Elements.

The concentration of some rare earth salts in a solution may be determined by measuring the thickness of the liquid layer, at which a certain characteristic band of that element just disappears, provided that the limiting concentration (or the thickness of liquid layer) of disappearance of the same band at the certain thickness of liquid layer (or at the certain concentration) is previously known.

According to my present study, this method of analysis is especially suited for such the rare earths, that show absorption bands in the ultra-violet region, because the latters are, as a rule, far more wide and distinct than those of the visible part. For example, cerous chloride absorbs selectively very wide region of spectrum in ultra-violet; its analysis by using this method, therefore, will be scarcely hindered by the presence of other rare earth salts, which absorb likewise selectively in ultra-violet. In applying Beer's law, it was calculated from the experimental results that the quantity of cerous chloride in a given solution may be determined even when its fifty times so much praseodymium and samarium salts and its hundred times so much lanthanum and neodymium salts are simultaneously presented in that solution. In the actual case of mineral analysis, if the total quantity of the salts of lanthanum, praseodymium, neodymium and samarium do not exceed hundred times of that of cerous salt, the latter will be conveniently and rapidly determined by this spectroscopic method in performing as follows: the fraction of cerium group extracted from a given mineral will be changed into chlorides and the absorption spectra of that solution in various thicknesses of liquid layer are photographed on a same plate. The absorption curve will then be traced according to the Hartley-Baly's system and the thickness of liquid layer at the bottom of the absorption curve is measured. On the other hand, the absorption curve of cerous chloride of the known concentration will be prepared for the purpose of comparison, and on this curve, the thickness of liquid layer at bottom of the same absorption band is likewise determined. According to the Beer's law, the following simple relation will be given to denote the concentration of cerous chloride in the mineral extract:

$$c' = \frac{c\,l}{l'}$$

where c and c' mean respectively the concentrations of known and unknown solutions of cerous chloride, and l and l' are respectively the thicknesses of liquid layer of these solutions, at which the absorption bands just disappear.

For the purpose of the verification of this method, the following experiment was carried out: a solution, containing 0.02 gr. CeO_2 and 1.1240 gr. R_2O_3 (R= metals of Ce-group, Ce itself excluded) in a litre as chlorides, was prepared, and the absorption spectrogram of this solution was made as usual. The absorption curve showed that the bottom of the band, the wave lengths of which is found 2469 Å, appears at the thickness of 4.0 cm. of liquid layer, while in the control solution, which contains 0.017 gr. of CeO_2 as chloride in a litre, the bottom of the same absorption band was found at the thickness of 4.8 cm. of liquid layer. The quantity of CeO_2 in the first solution will, therefore, be calculated from the following formula.

$$\frac{4.8 \times 0.0170}{4.0} = 0.0204.$$

As for the ultra-violet absorption of samarium chloride, it is not interfered by that of lanthanum chloride, but when the quantities of the coexisting neodymium and praseodymium chlorides exceed respectively 3 and 1 times of that of samarium chloride, the characteristic absorption band at 2600 Å of the latter salt is no more of without influence. In the practice, therefore, the spectrogram of the solution of rare earths fraction extracted from a certain mineral will be carefully examined, and if the band of samarium 2600 Å be found therein, so we can at least conclude that the extract contains neodymium in the less quantity than 3 times that of samarium and praseodymium less than the equal quantity of samarium. In this case, therefore, the above mentioned method may be applied for the quantitative analysis of the latter element utilising its characteristic band.

Summary

1) The absorption spectra of chlorides of lanthanum, cerium (trivalent), praseodymium, neodymium, Samarium and erbium were studied and compared with the works published up to the present time.

2) In studying the ultra-violet absorptions of these salts, the existence of the following bands was confirmed:

3350 and 2469 Å in cerous chloride; 2600 Å in samarium chloride; 2470 Å in erbium chloride.

3) A method for the quantitative analysis for cerium and samarium by measuring their characteristic ultra-violet absorptions was described.

I express my hearty thanks to Prof. Yuji Shibata for his kind advices.

The cost of the investigation was defrayed from the grant of the Department of Education.

Laboratory of Inorganic Chemistry,
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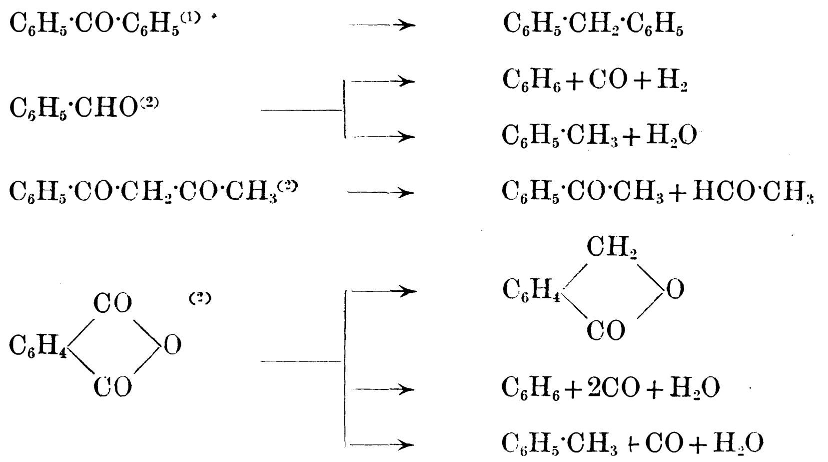
ON THE CATALYTIC HYDROGENATION OF THE CARBONYL GROUP IN AROMATIC COMPOUNDS UNDER PRESSURE IN THE PRESENCE OF COPPER. PART I.

By **Bennosuke KUBOTA** and **Taro HAYASHI.**

Received December 4, 1925. Published January 28, 1926.

It has been shown by P. Sabatier and his collaborators that the carbonyl group in aromatic compounds undergoes a violent hydrogenation in gaseous system in the presence of copper, giving rise to the formation of hydrocarbons or even to the scission of the molecule, and that it is impossible in general to get any alcohol from aldehyde or ketone by this process of hydrogenation.



$$C_6H_5{\cdot}CO{\cdot}C_6H_5{}^{(1)} \longrightarrow C_6H_5{\cdot}CH_2{\cdot}C_6H_5$$

$$C_6H_5{\cdot}CHO^{(2)} \longrightarrow C_6H_6+CO+H_2 \quad ; \quad \longrightarrow C_6H_5{\cdot}CH_3+H_2O$$

$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3{}^{(2)} \longrightarrow C_6H_5{\cdot}CO{\cdot}CH_3+HCO{\cdot}CH_3$$

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O^{(2)} \longrightarrow C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O \quad ; \quad \longrightarrow C_6H_6+2CO+H_2O \quad ; \quad \longrightarrow C_6H_5{\cdot}CH_3+CO+H_2O$$

On the other hand, Aloy and Brustier(3) have shown that borneol changes into camphor almost perfectly at 300° in the presence of this catalyst. These facts naturally lead one to suppose that, as copper is, under ordinary pressure, evidently a suitable catalyst for dehydrogenation of the carbinol group rather than for hydrogenation of the carbonyl group, the reverse reaction would take place under high pressure;

$$-CH(OH)- \rightleftarrows -CO- + H_2.$$

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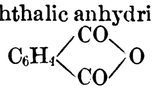
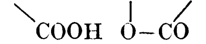
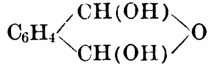
(1) P. Sabatier et Murat, *Compt. rend.*, 158 (1914), 761.

(2) P. Sabatier et B. Kubota, *Compt. rend.*, 172 (1921), 733.

(3) Aloy et Brustier, *Bull. Soc. Chem.*, 9 (1911), 733.

This view has been found to be correct from the following experiments. Diketones (benzil, benzoyl acetone, and phthalic anhydride) and monoketones (acetophenone, benzophenone and camphor) were hydrogenated in an autoclave by means of hydrogen under high pressure in the presence of this catalyst, all producing expected products. It was found, moreover, that two new compounds, methyl-(β-phenyl-β-oxy-ethyl)-ketone $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO \cdot CH_3$ and dioxyphthalane $C_6H_4[CH(OH)]_2O$, were obtained from benzoyl acetone and phthalic anhydride. The results may be summarized as follows:

	Substance	Temperature of the oil bath	Pressure (atm.) initial	Pressure (atm.) max.	Product
Diketone	Benzil $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$	100°	76	92	Benzoin $C_6H_5 \cdot CO \cdot CH(OH) \cdot C_6H_5$ Hydrobenzoin and Isohydrobenzoin $C_6H_5 \cdot CH(OH) \cdot CH(OH) \cdot C_6H_5$
		130	64	80	Hydrobenzoin and Isohydrobenzoin
	Benzoyl acetone $C_6H_5 \cdot CO \cdot CH_2 \cdot COCH_3$	83	68	79	Phenyl-(β-oxy-n-propyl)-ketone $C_6H_5 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CH_3$ Methyl-(β-oxy-β-phenyl)-ketone $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO \cdot CH_3$
		105°	57	69	α-Methyl-γ-phenyl-trimethylene glycol $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CH(OH) \cdot CH_3$
	Phthalic anhydride  $C_6H_4 \langle \begin{matrix} CO \\ CO \end{matrix} \rangle O$	120	67	82	Hydrodiphthalyl lactonic acid  $\begin{matrix} C_6H_4-CH_2-CH-C_6H_4 \\ COOH \quad O-CO \end{matrix}$ Dioxyphthalane  $C_6H_4 \langle \begin{matrix} CH(OH) \\ CH(OH) \end{matrix} \rangle O$
Monoketone	Acetophenone $C_6H_5 \cdot CO \cdot CH_3$	140	66	86	Phenyl-methyl carbinol $C_6H_5 \cdot CH(OH) CH_3$
		160	66	96	Phenyl-methyl-methane $C_6H_5 \cdot CH_2 \cdot CH_3$
	Benzophenone $C_6H_5 \cdot CO \cdot C_6H_5$	120	50	61	Diphenyl carbinol $C_6H_5 \cdot CH(OH) \cdot C_6H_5$ Diphenyl methane $C_6H_5 \cdot CH_2 \cdot C_6H_5$
		190	52	67	Diphenyl methane $C_6H_5 \cdot CH_2 \cdot C_6H_5$ Tetraphenyl ethane $(C_6H_5)_2 : CH \cdot CH : (C_6H_5)_2$
	Camphor $C_{10}H_{16}O$	120-150	10-90	19-101	Borneol and Isoborneol $C_{10}H_{18}O$

Experiments with diketones are described in this paper, and those with monoketones will be published in the next communication.

Experimental.

The substance to be hydrogenated was mixed intimately in a pyrex glass tube with about half its weight of fine copper of purple colour, which had been prepared from precipitated cupric hydroxide by the reduction with a very slow current of hydrogen at about 180°. It was placed in the autoclave, to which hydrogen under 60–76 atmospheres was introduced and was heated in an oil bath about 18–30 hours. When the reaction was completed, the whole mass in the pyrex glass tube was shaken up with either, and the ethereal solution was filtered from the catalyst. The solution, after being dehydrated over anhydrous sodium sulphate, was distilled to expel ether, and the product remaining in the flask was examined.

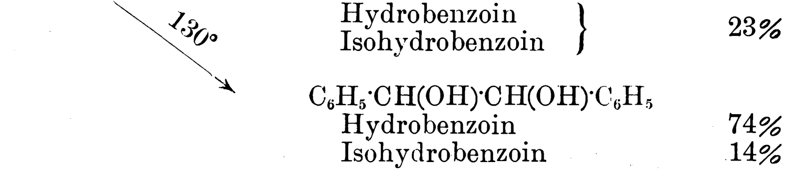
1. Benzil $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$.

Being treated at 100’ (the temperature of the oil bath) under 60 atmospheric pressure (initial) as above mentioned, the mixed product was treated with hot dilute alcohol and was filtered while still hot. Faintly yellow crystals were obtained, which melted at 132° and was identified as benzoin.

To this hot filtrate some hot water was added gradually so long as yellowish oil, which was proved to be unchanged benzil, separated out, and the hot solution was filtered off. When the filtrate was cooled, large crystals separated out. This was found to melt at 134–135° and to possess the characteristic properties of hydrobenzoin, its diacetate being formed by the action of glacial acetic acid on it at 170–180’ and so forth.

After filtering the hydrobenzoin, the volume of the filtrate was diminished by evaporation on a water bath, when some crystals of hydrobenzoin again separated out. This was filtered off while still hot and the filtrate was allowed to stand over night. Then some crystals separated out in needles. This substance melted at 94–95’ and proved to be isohydrobenzoin.

Similar experiments with benzil was undertaken at about 130° under 64 atmospheric pressure, the products were found to be hydrobenzoin and isohydrobenzoin. Thus the results obtained with benzil may be represented in the following scheme:



2. Benzoyl acetone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

This was treated at 83–87° (the temperature of the oil bath) under 68 atmospheric pressure (initial) as above mentioned. A large quantity of crystalline substance, which proved to be nothing but unchanged benzoyl acetone, and a colourless viscous liquid with a good smell were obtained. The liquid was filtered, fractionated under 12 mm. pressure, and the following fractions were collected: 125–135° (3%), 135–136° (30%), 150–153° (4%).

The first fraction was found to be nearly pure unchanged benzoyl acetone (melting point, 48°) dissolved in the liquid. The second fraction was shaken up with a dilute caustic soda solution so long as it showed any marked ferric chloride reaction, in order to elliminate a trace of benzoyl acetone. Then the liquid was extracted by means of ether. The ethereal solution, on being dehydrated over anhydrous sodium sulphate and evaporated, gave a liquid boiling at 134–136° under 10 mm. pressure, which on analysis proved to be a new oxyketone. (Found: $C=73.23$; $H=7.99$. $C_{10}H_{12}O_2$ requires $C=73.15$; $H=7.32$ per cent).

The liquid produced an yellow turbidity on the addition of a solution of phenylhydrazine in acetic acid, which precipitated together after a few hours. This was filtered and recrystallised from alcohol. It formed orange crystals melting with partial decomposition at 120–122°. (Found: $C=74.80$; $H=7.01$; $N=11.35$. $C_{16}H_{18}N_2O$ requires $C=75.59$; $H=7.14$; $N=11.01$ per cent).

When it was warmed for some time with acetyl chloride on a water bath, it turned into a colourless viscous liquid with a very good smell.

These facts show that the product is evidently an oxyketone, suggesting as its constitution either of the two following formulae:

$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$ (1), $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$ (2).

By the condensation of acetophenone with acetaldehyde, Staudinger and Kon⁽¹⁾ obtained a viscous liquid boiling at 150–153° under 12 mm. pressure, which proved to be phenyl-(β-oxy-n-propyl)-ketone (1). The properties of the third fraction were found to be in good agreement with those of the oxyketone of Staudinger and Kon.

It is now clear that the second fraction is a new oxyketone represented by the formura (2): $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

In the course of their investigation on catalytic hydrogenation of several aliphatic-aromatic carbonyl compounds in presence of palladium, Straus and Grindel⁽²⁾ have shown that the hydrogenation of those compounds in which the carbonyl group is in the α-position to the benzene ring is carried out more quickly than the other carbonyl compounds. Our result with benzoyl

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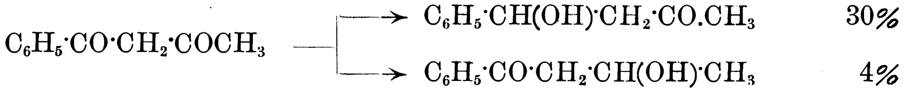
(1) Staudinger and Kon, *Ann.*, 384 (1911), 124.

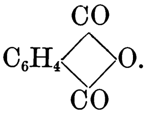
(2) Straus and Grindel, *Ann.*, 439 (1924), 276.

acetone is obviously in complete agreement with that of Straus and Grindel, being represented by the following scheme:

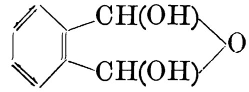


$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}COCH_3 \longrightarrow \begin{cases} C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO.CH_3 & 30\% \\ C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3 & 4\% \end{cases}$$

Benzoyl acetone was next treated at 105° under 57 atmospheric pressure. The product was a liquid which was fractionated under 12 mm. pressure and the following fractions were collected: 135–160° (very little), 162–166° (70%), 167–172° (25%). The properties of the second fraction were found to be in good agreement with those of α-methyl-γ-phenyl trimethylene glycol, $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$, of E. Bauer.(1)

3. Phthalic anhydride 

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O.$$

This was treated at 120° under 67 atmospheric pressure (initial) and the result was, that a large quantity of white crystals and some green viscous liquid were obtained. This was drained on a funnel with a perforated plate and the filtrate was shaken up with dilute hydrochloric acid when the green colour of the liquid disappeared. This was washed several times with a dilute sodium carbonate solution, then with water, and extracted with ether. The ethereal solution was dehydrated over anhydrous sodium sulphate and the ether was distilled off, when a colourless liquid was obtained. (Found: C=63.95; H=5.32. $C_8H_8O_3$ requires C=63.15; H=5.31 per cent). Thus it seems to us that this is a dioxyphthalane, 
which has not yet been obtained by any other reaction.

On being treated with benzoyl chloride and sodium hydroxide solution, it gave a viscous liquid which smelled fragrant and was ascertained by analysis to be dibenzoyl ester of dioxyphthalane. (Found: C=73.31; H=4.26. $C_{22}H_{16}O_5$ requires C=73.30; H=4.44 per cent).

The crystalline substance above described, on being recrystallised from alcohol, separated out in colourless plates melting at 197–198°. Its properties were found to be in good agreement with those of hydrophthalyl lactonic acid of Wislicenus.(2)

As it is known that the phthalic acid and its derivatives are apt to change into phthalic anhydride on being oxidised by air when heated, the

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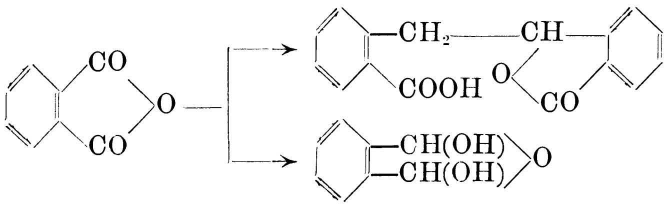
(1) E. Bauer, *Compt. rend.*, 154 (1912), 1093.
(2) Wislicenus, *Ber.*, 17 (1884), 2178.

dioxyphthalane and its benzoyl ester have not been distilled, because they will be decomposed into phthalic anhydride even under 5 mm. pressure.

Now the hydrogenation of phthalic anhydride by this process may be represented by the following scheme:



70% Hydrodiphthalyl lactonic acid of Wislicenus

12% Dioxyphthalane, a new compound.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.

ÜBER DIE ANHYDRISIERUNG VON AMINOSÄUREN UND PEPTIDEN. (EINE ANTWORT AN HERRN ABDERHALDEN.)

Von **Keita SHIBATA.**

Eingegangen am 14. Dezember 1925. Ausgegeben am 28. Januar 1926.

In einem kürzlich erschienenen Aufsatz(1) hat Herr Abderhalden unter Bezugnahme auf meine Veröffentlichung(2) über den Glycerin-Abbau der Eiweisskörper folgendes geschrieben: „Shibata glaubt, dass die Anwendung von Glycerin jede sekundäre Umlagerung ausschliesse......," und knüpfte daran die Beschreibung seiner Versuche über die Anhydridbildung aus einigen Di- und Tripeptiden durch Erhitzen mit Glycerin an. Es lag mir ganz fern eine ebensolche Behauptung aufzustellen, sodass ich genötigt bin, im folgenden einige Zeilen der Klarlegung der Sache zu widmen.

Was Herrn Abderhalden zur obigen unzutreffenden Bemerkung veranlasste ist wahrscheinlich folgender Satz(3) in meiner Mitteilung: „Da die oben beschriebene Methode(4) jede Möglichkeit der Hydrolyse ausschliesst, so ist es gar nicht an *sekundäre Entstehung* der Anhydride aus Aminosäuren

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(1) Emil Abderhalden u. Ernst Schwab: Z. physiol. Chem., 148, 254. (Oktober 1925.)

(2) Keita Shibata: Acta Phytochimica, 2, 39. (April 1925.)

(3) Daselbst, 43.

(4) d.h., Depolymerisierung der Proteine durch Erhitzen mit wasserfreiem Glycerin.

und Peptiden zu denken.“ Wie leicht ersichtlich, wollte ich damit meinen, dass die Anhydride nicht erst aus hydrolytisch abgespaltenen Aminosäuren und Peptiden hervorgegangen sind, sondern vorgebildet in Proteinkörper existieren müssen. Derselbe Gedankengang liegt bekanntlich auch der Isolierung der Polysaccharidgrundkörper durch Glycerinabbau zu Grunde.

Die interessante Beobachtung Maillards über die Anhydridbildung aus Aminosäuren durch Erhitzen im Glycerin wurde bereits von mir bei der Darstellung von eiweissähnlichen kolloiden Polymeren benützt, wie in meiner oben zitierten Mitteilung angegeben.(1) Weiterhin sind die Versuche zur Herstellung verschiedener Diketopiperazinderivate nach der Maillardschen Methode schon lange von Dr. Teiichi Asahina in Angriff genommen, mit dem Zweck, die Identifizierung und Kennzeichnung der Proteingrundkörper zu erleichtern.

Selbstredend führen ich und meine Mitarbeiter weitere Untersuchungen in der schon angekündigten Arbeitsrichtung ungestört aus.

* * *

Bei dieser Gelegenheit möchte ich nochmals kurz auf die oben erwähnten eiweissähnlichen Substanzen hinweisen, die beim Erhitzen des Aminosäurengemisches mit wenig Glycerin entstehen.(2) Die betreffende Substanz wird, wie schon angegeben,(3) aus der alkoholischen Glycerinlösung beim Zusatz von kleinen Mengen von Oxyden, Neutralsalzen (Chloriden, Nitraten, Acetaten) sowie gewissen Komplexsalzen der Erdalkalimetalle(4) in voluminösen Flöckchen niedergeschlagen, und durch Waschen mit abs. Alkohol und Trocknen im Vakuum in der Form eines hellgelben amorphen Pulvers gewonnen. Die Substanz ist im Wasser spielend leicht löslich, enthält keine freie Aminosäuren, gibt nicht nur verschiedene Farben-,

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(1) Dort (S. 45) schrieb ich: „Die oben dargestellten Versuche kann man auch mit freien Aminosäuren anstellen, da die letzteren, wie Maillard nachwies, beim Erhitzen im Glycerin in Anhydride übergeführt werden und dabei aus dem Gemisch zweier Aminosäuren auch ein ‚gemischtes‘ Anhydrid entsteht.“ Dass die Peptide dabei wie Aminosäuren verhalten, ist ja von vornherein zu erwarten.

(2) Die Association (Polymerisation) und Deassociation der Anhydriden im Glycerin stellen gewissermassen einen reversiblen Vorgang dar, der sich nach Konzentration, Temperatur und anderen Faktoren richten.

(3) K. Shibata: loc. cit., 45.

(4) Die Salze von Schwermetallen (Mn, Fe, Ni, Co, Zn, Cd, Cu, Ag, Hg) und Lanthan lassen sich ebensogut wie die von Erdalkalien dazu verwenden, aber die entstehenden Produkte sind oft im Wasser schwer oder kaum löslich. Die Verbindungen von Alkalimetallen sowie Mg, Be, Al u.a. sind nicht zum Versuch brauchbar.

sondern auch Fällungsreaktionen der Proteinkörper. Die prozentische Zusammensetzung variiert freilich nach dem Mengenverhältnisse der angewandten Aminosäuren. Der Aschengehalt der Präparate lässt sich auf Anlagerungsverbindungen der Metallsalze mit den polymeren oder assoziierten Anhydriden(1) schliessen. Aber die Substanzen können von Metallen weitgehend befreit werden, indem man, z. B., die letzteren in ammoniakalischer Lösung als Karbonate ausfällt, und aus dem Filtrat gewinnt man durch Alkoholfällung eine beinah aschefreie Substanz zurück. Die Entstehungsbedingungen und Eigenschaften dieser künstlichen pepton- oder albumoseartigen Substanzen werden a.a.O. näher beschrieben.

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(1) Oder deren tautomeren Formen.

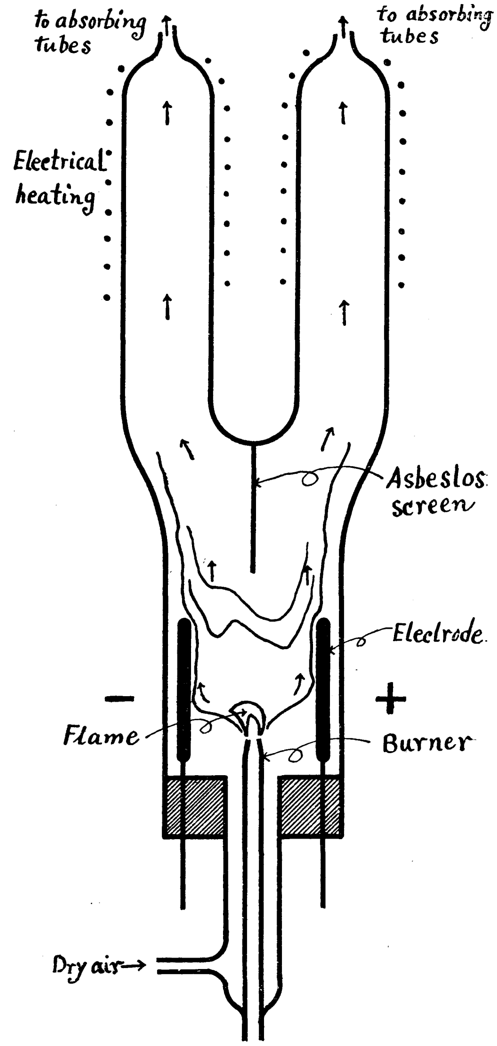
DEFLECTION OF A FLAME IN THE ELECTRIC FIELD.(1)

By Yuzaburo SHIBATA.

Received November 4, 1925. Published February 28, 1926.

It is well known that(2) a flame deflects itself when it is brought into an electric field. This fact can be explained as the result of the migration of the oppositely charged ions of a flame in different directions in an electric field. So we can catch differently charged particles in separate vessels and analyse them.

Ordinary Coal Gas Flame. If we put a small non-luminous flame of an ordinary coal gas burner in an electric field, the visible part of the flame is deflected towards the negative pole. But the flow of the hot gas produced by the flame streched itself almost symmetrically towards both electrodes. This fact can easily be observed by its shadow on a screen projected by strong illumination. The following experiment has been carried out to study the chemical compositions of the different parts obtained by electrical deflection.



A small ordinary coal gas flame is burnt in a two wayed glass cylinder as shown in the accompanying figure, the electric field being applied by a Wimshurst machine. Then the hot gases which was splitted by the field will go up

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(1) Read before the Chemical Society of Japan, December 5, 1925.

(2) J. J. Thomson, Conduction of Electricity Through Gas. 1906, page 230.

separately along the two ways. By use of the tubes of calcium chloride and soda lime, the relative amounts of carbon dioxide and water were determined in each portions. The results are shown in the following table, together with the blank tests.

Electrode	Carbon dioxide	Water vapour	$\frac{CO_2}{H_2O}$	Ratio
	gr.	gr.		
Left (+)	0.494	0.341	1.45	1.02
Right (−)	0.615	0.415	1.48	
Left (+)	0.855	0.604	1.42	1.05
Right (−)	0.953	0.642	1.49	
Left (+)	0.519	0.375	1.39	1.02
Right (−)	0.560	0.396	1.42	
Left (−)	1.353	0.982	1.38	1.03
Right (+)	1.243	0.930	1.34	
Left (−)	0.825	0.551	1.50	1.04
Right (+)	0.553	0.385	1.44	
Left (−)	0.269	0.2095	1.28	1.04
Right (+)	0.177	0.143	1.24	
Left (no field)	0.2595	0.1675	1.55	1.00
Right (no field)	0.1865	0.1205	1.55	
Left (no field)	1.064	0.6375	1.67	1.00
Right (no field)	0.804	0.4825	1.67	

As seen from the above table, carbon dioxide is always in excess at the negative electrode than at the positive. The reason of this fact might be explained as follows. The molecules of a gas will split up into atoms or atomic groups in the intermediate stages of combustion, and some of the atoms or the atomic groups thus formed will be charged. It is probable that the carbon atom or the atomic groups CH, CH_2 CH_3 etc. have the positive charges, for the glowing carbon particles of a luminous flame in an electric field are strongly attracted to the negative electrode.

Flame Containing Sodium Chloride Vapour. In this case the sodium atom is supposed to be charged positively, and the chlorine atom negatively. This has been shown by the following experiment. When small silver plates are placed perpendicular to the electric field at a small distance from the flame at each side on the electrode, a purplish white deposit of silver chloride is seen on the surface of the silver plate on the side of the positive electrode, notwithstanding that the flame is deflected to the negative electrode as a whole.

Flame Containing Cupric Chloride. The flame has been obtained by blowing the ammoniacal solution of cupric chloride into the coal gas flame. In this case the copper atom is charged positively, and the chlorine atom negatively, which has been shown by a similar experiment as above. Reddish deposit of copper was seen at the negative electrode, while whitish deposit of silver chloride at the positive electrode.

The auther's thanks are due to Prof. Sameshima for his kind guidance.

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THE MOLECULAR ASSOCIATION OF PHENOL IN BENZENE AND WATER.

By **Kwantaro ENDO.**

Received November 29, 1925, Published February 28, 1926.

It has already been discussed by many investigators(1) that the partition coefficient of phenol between benzene and water is not constant but varies with its concentration, although the problem has not yet been solved. H. Hirobe(2) studied the partition of phenol between chlorobenzene and water, and reached the conclusion that in chlorobenzene there exists the chemical equilibrium,

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3,$$

while in water only the monomolecular phenol is present. As benzene is very similar in chemical natures to chlorobenzene, we may expect the same conclusion in the case of benzene. Following experiments were undertaken from this point of view.

I. Partition of Phenol between Benzene and Water at 25°C.

The measurements of the partition coefficient were carried out at 25° in the usual manner. Specially purified phenol and benzene were employed. Phenol was determined by the bromine method which was tested and found very satisfactory. The results are shown in Table 1, where W and B represent the molar concentrations of phenol calculated as C_6H_5OH in the aqueous and in the benzene layer respectively.

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(1) Rothmund and Wilsmore, *Zeit. physik. Chem.*, **40** (1902) 611.
W. Vaubel, *J. prakt. Chem.*, **67** (1903) 473.
James C. Philip and C.H. Douglas Clark, *J. Chem. Soc.* **127** (1925) 1274.

(2) H. Hirobe, *J. Coll. Science Imp. Univ. Tokyo*, **25** (1908) Art. 12.

TABLE 1.

Molar Concentrations of Phenol in		Partition Coeff.
Benzene Layer B	Aqueous Layer W	$P=\frac{W}{B}$
1.0442	0.2372	0.2272
0.7803	0.2052	0.2630
0.5437	0.1645	0.3026
0.2422	0.0934	0.3855
0.1177	0.0501	0.4256

Thus the values of P decrease with increasing concentration, as other investigators have already found.

At first, we assume that the following equilibrium is established in the benzene layer,

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3$$

while only single molecules of phenol are present in the aqueous layer. Let c_1 and c_3 represent the molar concentrations in benzene of C_6H_5OH and $(C_6H_6O)_3$ respectively, then by the law of mass action,

$$Kc_1^3=c_3,$$

where K denotes the association constant. Moreover, there is the relation,

$$B=c_1+3c_3=c_1+3Kc_1^3.$$

Now by the law of partition the ratio of c_1 and W is to be constant; so

$$\gamma W=c_1$$

where γ is the real partition coefficient of C_6H_5OH between benzene and water.

Then, $$B=\gamma W+3\gamma^3KW^3 \cdots\cdots\cdots(1)$$

or $$B/W=1/P=\gamma+3\gamma^3KW^2 \quad (2)$$

If we plot $1/P$ as ordinate and W^2 as abscissa, then we must obtain a straight line, providing our assumption is correct. Figure 1 which shows quite a straight line, has been drawn in such a manner. The equation (2), therefore, is correct and consequently our assumption is right.

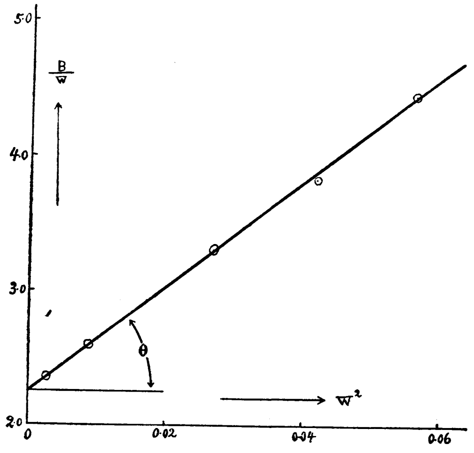

Fig. 1.

In the next place, we can find the values of γ and K from Fig. 1, thus

$$(1/P)_{W=0}=\gamma=2.25$$

and

$$\tan\theta=\frac{d(1/P)}{d(W^2)}=3\gamma^3K=37.77$$

I have calculated these values more exactly by the method of the least squares and obtained

$$3\gamma^3K=37.71 \quad \text{and} \quad \gamma=2.272$$

Then $K=1.072.$

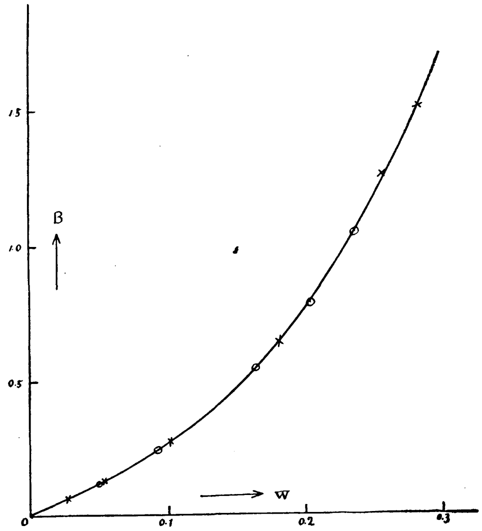

Fig. 2.

So the equation (1) becomes

$$B=2.272\,W+37.71\,W^3 \quad \cdots\cdots\cdots\cdots\cdots(3)$$

The curve in Fig. 2 has been drawn by the equation (3) and the circlets denote the points observed by the author, and the crosses by Rothmund and Wilsmore. The agreement between the theory and the experiment is quite satisfactory.

II. Depression of the Freezing Point of the Aqueous Phenol Solution.

The cryoscopic experiments were also done in order to determine the molecular states of phenol in water. The experiments were carried out on a larger scale than the ordinary cryoscopic method to get the greater accuracy. About 500 cc. of solution have been used each time. The results are shown in Table 2, where C denotes the molar concentration of phenol calculated as C_6H_5OH.

They are also shown graphically in Fig. 3, which represents a d–C curve. If the Raoult's law holds, d–C curve must be a straight line represented by the equation $d=kC$, $(k=1.86)$. But as we see in Fig. 3, it is not a straight line, though the deviation is not large. It shows a regular downward deviation which suggests that there occurs an association of phenol

TABLE 2.

Weight of Water in gram w.	Weight of Phenol in gram g.	$C=\frac{1000g}{94.048w}$	Depression of Freez. Pt. in degree d.
499.4	18.8698	0.4016	0.676
499.4	14.2540	0.3034	0.524
499.4	10.7330	0.2284	0.407
499.3	8.4313	0.1795	0.325
499.4	5.7585	0.1226	0.228
499.4	4.0364	0.0859	0.165
499.4	2.6505	0.0564	0.110
499.3	2.4515	0.0522	0.101

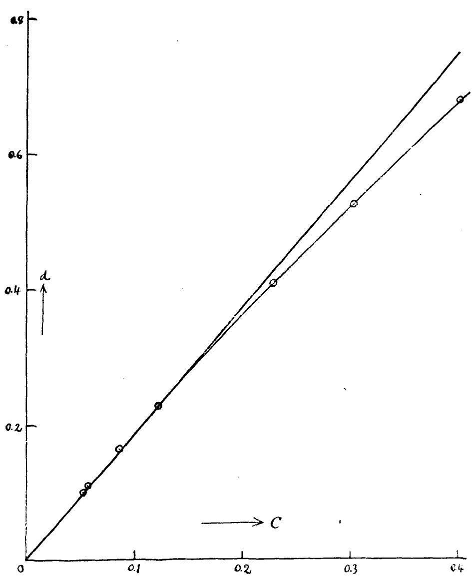

Fig. 3.

in a small degree in concentrated solutions. Generally, the degree of association decreases with the elevation of the temperature. So at 0°C. the association of phenol is perceptible when the molar concentration is greater than 0.2, while in more dilute solutions it can safely be assumed that there is no association as has been stated in the partition experiment.

Now we will assume

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3$$

in aqueous solution at 0°C. If c_1' and c_3' denote the molar concentrations of C_6H_5OH and $(C_6H_6O)_3$ respectively, then

$$K'c_1'^3=c_3',$$

where K' is the association constant of phenol in water. The analytical concentration C becomes

$$C=c_1'+3c_3',$$

and the depression of freezing point must be expressed by

$$d=k(c_1'+c_3').$$

Therefore, $C-\frac{d}{k}=2c_3'$ or $c_3'=\frac{1}{2}\left(C-\frac{d}{k}\right)\cdots\cdots(4)$

and $$c_1' = \frac{d}{k} - c_3' \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

By using these two equations we can calculate c_1' and c_3' from Fig. 3 or directly from the observed data. We can also calculate the value of $K' = c_3'/c^3_1'$.

As we see in Fig. 3 the experimental points at concentrations lower than $C = 0.2$ almost coincide with the theoretical line of Raoult, so this part has been excluded from the calculation. The results are shown in Table 3.

TABLE 3.

C	d	d/k	c_3'	c_1'	K'
0.4000	0.673	0.3618	0.0191	0.3427	0.47
0.3500	0.596	0.3204	0.0148	0.3056	0.52
0.3000	0.519	0.2814	0.0093	0.2721	0.46
0.2500	0.441	0.2371	0.0065	0.2306	0.53
0.2000	0.359	0.1930	0.0035	0.1895	0.51
			Mean $K' = 0.50$		

The constancy of K' is satisfactory.

Summary.

1. From the measurement of the partition coefficient of phenol between benzene and water, it has been proved that phenol is in the state of chemical equilibrium

$$3C\,H_5OH \rightleftarrows (C_6H_6O)_3$$

in the benzene layer at 25°C.

2. From the measurement of the freezing point of the aqueous phenol solution, it has also been proved that phenol is in the chemical equilibrium similar to the above in the aqueous solution at 0°C.

It is to be emphasized that phenol associates itself in tripple molecules and not in double molecules.

My best thanks are due to Professor K. Ikeda for his kind guidance in the present experiments.

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THE HEATS OF FUSION OF SOME ORGANIC SOLVENTS WHOSE MELTING POINTS ARE RELATIVELY LOW.

By **Shinroku MITSUKURI.**

Received November 30, 1925. Published February 28, 1926.

The heats of fusion of organic solvents, whose melting points are relatively low, have scarcely been measured up to the present. O. Maass and L. J. Waldbauer⁽¹⁾ measured the heat capacities of several organic solvents between various points at low temperatures and at room temperature, and thence calculated their heats of fusion. E. Beckmann and his co-workers⁽²⁾ measured the lowerings of freezing points of solutions in organic solvents and calculated the heats of fusion of those solvents by the van't Hoff's formula.

The present author also determined the lowerings of the freezing points of the solutions, and thence calculated the heats of fusion of several solvents by a thermodynamical formula. He, however, constructed an apparatus of new design, which was specially suitable for the determination of the melting points with a relatively small quantity of the samples.

I. The Apparatus and the Method of the Experiment.

The relation between the freezing point and the concentration of a solution is given by the following formula, which can be proved thermodynamically : that is,

$$\frac{d\ln N}{dT}=\frac{Q}{RT^2} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where N is the molar fraction of the solvent and Q is the heat of fusion of the solvent at the freezing point of the solution, T. Now, if the range of temperature is small and Q is taken as constant over this range, formula (1) can be integrated to the following :

$$\ln\frac{N}{N'}=\frac{Q}{R}\left\{\frac{1}{T'}-\frac{1}{T}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots(2)$$

where T and T' are the freezing points of the solutions with the concentrations N and N' respectively. By this formula, the heat of fusion of the

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(1) Maass & Waldbauer, *J. Am. Chem. Soc.*, 47 (1925), 1.

(2) Beckmann & Waentig, *Z. anorg. allgem. Chem.*, 67 (1910), 17.
Beckmann & Faust, *Z. physik. Chem.*, 89 (1915), 249.

solvent can be calculated from the freezing points of two solutions at different concentrations.

It is general, however, that a pretty large quantity of the sample is necessary to determine the freezing points of organic solvents, because they are easy to supercool. The present author, therefore, cools the sample once down to the temperature where it perfectly solidifies, thence heats it up, and takes the point, where its melting finishes, as the temperature the same as the freezing point of the solution. Solid organic matters, however, are generally bad conductors of heat, and they can not be maintained at uniform temperature throughout all their parts during the heating, and consequently they can not melt at the same moment when they are heated. To overcome this difficulty, the present author designed the metal vessel shown in Fig. 1.

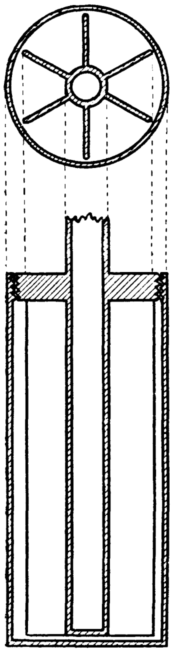

Fig. 1.

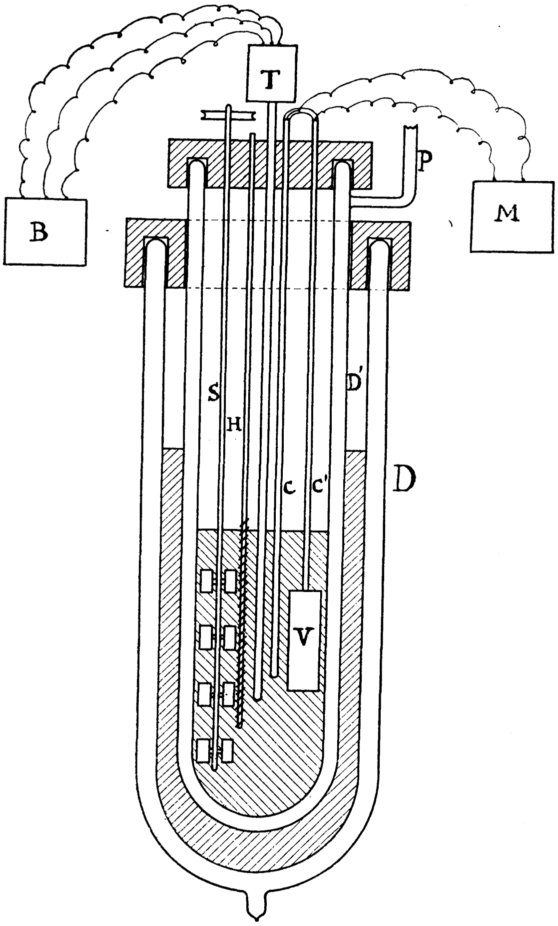

Fig. 2.

It consists of a cylindrical outer part and radial partition inside, whose function is to make heat conduction good so that the whole sample is maintained at the uniform temperature as far as possible. All the part of the vessel are made of brass, and the inner side is electrically coated with silver.

The whole apparatus is shown in Fig. 2. D is a large Dewar vessel, inside of which a double walled glass vessel D′ is placed ; the space between the double walls of this vessel is connected to a vacuum pump by the pipe P. V is the vessel for the sample shown in Fig. 1, in the middle hole of which one end of the thermocouple, C′, is inserted, the other end of it, C, is placed quite near to V. CC′ is an 8 series copper-constantan thermocouples, whose potential difference between C and C′ is measured by a millivoltmeter with 1/10 millivolt scale, M, and whose E.M.F. is 0.24 m.v. per degree centigrade. T is a platinum-resistance thermometer of about 2.5 ohms at 0°C., the resistance of which is measured by the bridge B, made by Leeds & Northrup Co, specially for the use with a resistance thermometer. By uniting these two the temperature can be measured with the precision of 1/100 degree centigrade. Inside the vessel D′, ether or pentane is put in, and this is stirred with the stirrer S to maintain a uniform temperature. H is a heater made of a coil of resistance wire, which is used for heating the liquid electrically.

The sample is put in the vessel V, the cover screwed in, sealed with water-glass, and then the vessel is placed in the liquid in D′. The space between the double walls of D′ is then filled with air to make heat conduction from the outside to the inside of the vessel good, and then liquid air is poured into D to cool the inside of D′. When the temperature of the liquid is about 20° below the point where the sample perfectly solidifies,—this is indicated by the cooling curve,—the vessel D is lowered so that D′ is out of the liquid air. Adjusting the electric current in the heater H and the degree of vacuum within the double walls, the heating rate inside D′ is regulated optionally. In this experiment the rate of 1.0—1.3 degree/minute is used. The temperature of the liquid in D′, which is measured by the thermometer T, is taken on abscissa and the E.M.F. of the thermocouple CC′, which corresponds to the temperature difference between the outside and the inside of V, is taken on ordinate, a curve is obtained. As the heat is absorbed at the region where fusion takes place, the temperature difference indicated by ordinate increases, and the curve ascending in this part, and when the heat absorption ends, the temperature difference again decreases and the curve descends ; thus it shows a maximum. The temperature where the extensions of the curve before and after the maximum intersect, minus the temperature difference corresponds to the maximum of the curve, is taken as temperature where fusion ends, that is the freezing point. Of course, this temperature may not indicate the true freezing point, but as the quantity which is needed is not the absolute values of the temperature, but the difference of the temperatures, no correction on this deviation is necessary.

II. The Results of the Experiment.

The materials used were all specially purified in this laboratory from the pure chemicals of Kahlbaum.

The results are tabulated in the following tables.

Solvent	Solute	Mol. % 100 N.	Melt. pt. T.	$\frac{1}{T}$	log N
Chloroform	—	100.00	211.59	0.004726	0.0000
	Toluene	97.73	211.09	0.004739	− 0.0100
	Acetone	96.78	210.50	0.004750	− 0.0142
	Toluene	95.13	210.00	0.004762	− 0.0217
	Ether	94.08	209.31	0.004777	− 0.0265
	Acetone	90.80	207.91	0.004810	− 0.0419
Acetone	—	100.00	179.37	0.005575	0.0000
	Toluene	98.28	178.67	0.005597	− 0.0075
	Toluene	97.66	178.19	0.005612	− 0.0103
	Toluene	94.18	176.51	0.005665	− 0.0260
	Ether	92.88	175.73	0.005691	− 0.0321
Carbon-bisulphide	—	100.00	162.30	0.003161	0.0000
	Toluene	98.35	161.02	0.006211	− 0.0072
	Toluene	97.43	160.33	0.006237	− 0.0113
	Toluene	93.93	157.30	0.006357	− 0.0272
Ethyl-ether	—	100.00	150.61	0.006640	0.0000
	Acetone	98.78	150.41	0.006650	− 0.0053
	Acetone	97.37	149.53	0.006688	− 0.0116
	CS_2	96.15	149.53	0.006688	− 0.0170
	Methyl-alc.	95.86	149.34	0.006696	− 0.0184
	Acetone	95.12	148.85	0.006718	− 0.0217
Methyl-alcohol	—	100.00	177.40	0.005637	0.0000
	Ether	98.92	176.17	0.005676	− 0.0047
	Toluene	96.84	173.81	0.005753	− 0.0139
	Acetone	96.62	173.52	0.005763	− 0.0148
	Toluene	95.96	173.13	0.005776	− 0.0179
Ethyl-alcohol	—	100.00	157.93	0.006332	0.0000
	CS_2	99.11	157.25	0.006359	− 0.0039
	Methyl-alc.	97.83	156.37	0.006395	− 0.0094
	Methyl-alc.	97.04	155.59	0.006427	− 0.0131

If the formula (2) holds in the solutions investigated, the points on the diagrams in which $\log N$ and $\frac{1}{T}$ are taken as co-ordinates are to be on straight lines for each solvent. As the values in the above table nearly satisfy this condition, the heats of fusion of the solvents can be calculated by the formula from the values of two points on these straight lines. The results of the calculations are as follows:

Solvent.	Heat of fusion.
Chloroform	2080 calories.
Acetone	1300
Carbon-bisulphide	660
Ethyl-ether	1400
Methyl-alcohol	600
Ethyl-alcohol	650

The heat of fusion of chloroform was given by Beckmann and Faust as 2100 cal., which coincides with that of ours.

The heats of fusion of acetone and methyl-alcohol were given by Maass and Waldbauer as 1140 cal. and 520 cal., respectively, which are smaller than those of ours, but perhaps it is better to say that they concide with each other within experimental errors.

The heat of fusion of ethyl-ether was given by Beckmann and Waentig as 2030 cal. which is much larger than that of ours.

Summary.

An apparatus which is suited to determine the lowering of freezing point of organic solvents was described.

The lowerings of the freezing points of the solutions of chloroform, acetone, carbon-bisulphide, ethyl-ether, methyl-alcohol and ethyl-alcohol were determined, and their heats of fusion were calculated.

This paper is a brief abstract of the following papers:

The heats of fusion of chloroform, acetone and carbon-bisulphide. by S. Mitsukuri and S. Aoki.

The heats of fusion of ethyl-ether, methyl-alcohol and ethyl-alcohol. by S. Mitsukuri and K. Hara.

which are going to be published in the Science Reports of the Tohoku Imperial University. The full description of the experiments and some discussions on the results are to be found in the above papers.

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CATALYTIC ACTION OF REDUCED COPPER ON OXIMES (ON BECKMANN'S REARRANGEMENT, XV.)

By Shozo YAMAGUCHI.

Received December 18 1925.   Published February 28 1926.

In the previous article(1) on this subject, the writer has stated that benzaldoximes when passed on reduced copper heated at 200° in an atmosphere of hydrogen were transformed into benzamide, benzonitrile and benzoic acid. The same experiment was extended to some aldoxime and ketoximes to draw some general conclusion from the experimental results, which might have an intimate connection with the explanation for the mechanism of Beckmann's rearrangement.

I. Furfuraldoxime.

20 gr. of the oxime, m.p. 89°, prepared according to the directions suggested by H. Goldschidt and E. Zanoli(2), were passed with hydrogen on reduced copper heated to 200°, and 2.8 gr. of solid and 4.5 gr. of liquid reaction products were obtained.

(A) Pyromusic Acid Amide.

The solid reaction product described above, was washed well with absolute ether, and then the amide, insoluble in ether, was recrystallised from hot alcohol in white beautiful crystals which melted at 141°–142°. The yield was 1.2 gr. It shows a blue colour, when treated with bromine water and caustic soda solution, as was mentioned by Saunders,(3) which on standing, changed to violet and then to red.

On analysis, it gave the following results :

0.1121 gr. subst. gave 0.2225 gr. CO_2 and 0.0528 gr. H_2O
0.1276 gr. subst. gave 14.6 c.c. N_2 at 23.5° and 750.2 mm.

	C	H	N
Found :	C=54.13	H=5.27	N=12.81
Calc. for $C_5H_5O_2N$:	C=54.04	H=5.54	N=12.60

The compound seems, so far as studied, to be identical with pyromusic acid amide. For the confirmation, it was converted into the bromoderivative following the direction given by Saunders, and this substance melted at about 125° with decomposition, and gave the following analytical results :

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Uni., A,* 9 (1925) 33.

(2) *Ber. D. Chem. Ges.,* 25 (1892) 2573.

(3) *Am. Chem. J.,* 15 (1893) 135.

0.2416 gr. subst. gave 0.4183 gr. AgBr.
Found : Br=73.68
Calc. for $C_5H_5O_2NBr_4$: Br=74.21

(B) The Acidic and the Basic Substances.

The liquid reaction product (4.5 gr.) was combined together with the ether washing of the solid reaction product, and dry ammonia gas was passed into the mixed solution to isolate the acidic substance, when a small quantity of the ammonium salt of an acid was separated, but further study of its chemical nature was not possible owing to the modicum of the sample. The ethereal solution separated by filtration from the ammonium salt, was evaporated to dryness to get rid off the solvent, and the residue was treated with a mixture of ether and hydrochloric acid solution to separate the neutral substance from the basic one. To the acid solution a platinum chloride solution was added and a platinum double salt was obtained.

(C) The Neutral Substance.

From the neutral ethereal solution separated from the acidic solution, furfural was isolated in the usual way, and confirmed to be so from its boiling point and the colour reaction.

II. Benzamidoxime(1).

4.5 gr. of the oxime, m.p. 76°–77°, were passed on reduced copper heated to 200° in an atmosphere of hydrogen, and 1.9 gr. of solid and 1.3 gr. of liquid reaction products were obtained.

(A) Benzamide.

It was isolated, in white crystals, m.p. 126°, from the solid reaction product, by treating it with absolute ether and then dilute alcohol. The yield was 1.2 gr. It was analysed and the following results were obtained :

0.1188 gr. subst. gave 0.2991 gr. CO_2 and 0.0638 gr. H_2O.
0.1312 gr. subst. gave 0.15016 gr. N_2 (by Kjeldahl's Method).

Found :	C=68.62	H=6.009	N=11.43
Cal. for C_7H_7ON :	C=69.39	H=5.82	N=11.57

(B) The Acidic and the Basic Substances.

The liquid reaction product and the ethereal washing of the solid reaction product were combined together, and an acidic, basic and a neutral substances were isolated from the mixed solution by treating with dry ammonia gas, and then with hydrochloric acid successively. The acidic substance which separated in the form of an ammonium salt, amounting to 0.4 gr., was identified to be benzoic acid from its melting point (121°) and from other chemical properties, after the salt was converted into a free acid and purified.

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(1) Tiemann, *Ber. D. Chem. Ges.*, 17 (1884) 128.

The basic substance was found to consist of a modicum of the reaction product.

(C) The Neutral Substance.

The neutral reaction product obtained in a liquid state, amounted to 0.6 gr., and was confirmed to be composed mostly of benzonitrile by subjecting it to reduction with metallic sodium and alcohol, and a trace of a basic substance was detected in the product.

III. Cinnamylaldoxime.

The oxime used in this experiment was prepared, according to the direction given by O. Brady and C. Thomas⁽¹⁾, from 20 gr. of cinnamylaldehyde, b.p. 125°–138°, 12 mm., and 15 gr. of hydroxylamine hydrochloride, and purified by crystallisation from benzene. It melted at 126°, and its yield was 16 gr.

16 gr. of the oxime were passed with pure hydrogen on finely divided copper heated at 200°, and obtained a tar-like substance and 6.8 gr. of a liquid reaction product. In order to isolate the acidic substance from the reaction product, dry ammonia gas was passed into its ethereal solution, but no precipitate appeared. It was then treated with hydrochloric acid to separate the basic substance from the neutral one.

The neutral substance was isolated in an oily form from the hydrochloric acid solution by extracting it with ether as usual. The yield was 1.1 gr. On standing it for a few days some crystals were separated from the oily matter, and it was confirmed that this was composed of cinnamic acid from its melting point of 132°–133°, and from its reaction. The oily residue separated from cinnamic acid was supposed, from the analogy of other cases, to be a mixture of cinnamyl aldehyde and the nitrile, but their presence could not be confirmed owing to the small amount of these substances (0.1 gr.)

Lastly, a resinous matter which remained with the copper in a reaction tube, was regarded as being formed by polymerisation of the reaction products mentioned above, though the chemical test for its confirmation was lacking.

IV. Di-benzyl Ketoxime.

8 gr. of di-benzyl ketoxime⁽²⁾ which melted at 119°-120° were passed with hydrogen over reduced copper at 200°, and 1.9 gr. of pasty substance and 1.1 gr. of liquid were obtained. The former was treated with absolute ether and then recrystallised from hot water, and colourless crystals which

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(1) *J. Chem. Soc.*, **121** (1922) 2103.

(2) *Ber. D. Chem. Ges.*, **21** (1888) 1316.

melted at 155° were obtained. The yield was 0.2 gr.

0.0919 gr. subst. gave 0.00958 gr. N_2 (by Kjeldahl's method).
Found: N=10.42, Calc. for C_8H_9NO: N=10.37.

The chemical properties and the analytical results agree well with those of phenylacetamide. The oily reaction product and the ether washing of the solid one were combined together, and acidic and neutral substances were isolated as usual.

The acidic substance was separated from the reaction product mentioned above, by means of ammonia in the form of an ammonium salt, then decomposed into free acid by means of hydrochloric acid, and was identified as phenylacetic acid from its melting point 76°–77°.

The neutral substance amounting to 2.6 gr. was subjected to distillation under 757 mm. and the following fractions were obtained:

Fraction	85°–120°	120°–130°	residue.
Yield	0.8 gr.	1.2 gr.	trace.

The second fraction was composed of liquid and solid substances, and the latter was separated by filtration, the liquid was supposed to be a mixture of 92% di-benzyl ketone and 8% benzyl nitrile by the nitrogen determination.

0.1205 gr. of the mixture gave 0.00154 gr. N_2 by Kjeldahl's method, whence it contains 0.00116 gr. of the nitrile. The existence of the ketone was confirmed by oximiration with hydroxylamine.

V. Benzophenone oxime.

14 gr. of the oxime were passed on reduced copper at 200° in an atmosphere of hydrogen, and 6.8 gr. of a liquid, and 0.3 gr. of a pasty substance were obtained.

From these reaction products trace of both acidic and basic substances could be isolated, but further confirmation of them was lacking owing to the small yield of the materials.

The neutral substance composed the larger part of the reaction products, and from this a crystalline substance was isolated through an alcohol solution, which melted at 202°–205°. The yield was 0.2 grm. It was soluble in hot benzene and chloroform. On analysis, it gave the following results:

0.1233 gr. subst. gave 0.4206 gr. CO_2 and 0.0765 gr. H_2O.

Found:	C=93.03	H=6.94
Calc. for. $C_{26}H_{22}$:	C=93.36	H=6.65

It was, thus, supposed to be a substance identical with tetraphenylethane.

To the alcoholic solution separated from the hydrocarbon, 4 gr. of hydroxylamine hydrochloride and 6 gr. of caustic soda were added to separate some benzophenone, and the mixture was left to stand for 4 hours, and then the solvent was distilled off from the reaction products. 2.2 gr. of benzophenone oxime and a hydrocarbon were obtained.

The latter substance amounting to 4 gr., boiled at 135°–140°, 10 mm., melted at 27°. On analysis, it gave the following results:

0.1583 gr. subst. gave 0.5367 gr. CO_2 and 0.0930 gr. H_2O.
Found: $C=92.47$ $H=6.57$
Calc. for. $C_{13}H_{12}$: $C=92.81$ $H=7.19$

It was, thus, confirmed to be diphenyl methane.

In another experiment, 20 gr. of benzophenone oxime were passed with pure hydrogen over reduced copper heated at 200°, and 10 gr. of a liquid reaction product was obtained in a receiver cooled below 0° with a freezing mixture, and the product was immediately treated with absolute ether. To the ethereal solution dry hydrochloric acid gas, after drying with anhydrous sodium salphate, was passed, whereas hydrochloride was separated, filtered, and washed well with absolute ether. The hydrochloride, thus obtained, amounting to 0.5 gr. was supposed to be a mixture of the hydrochlorides of amine, ketimine and ammonia, and the hydrochloride of diphenylketimine was separated from the other constituents and purified by the method of Hantzsch and Kraft⁽¹⁾. The yield was 0.1 gr.

The physical and chemical properties of the hydrochloride agreed well with those of the ketimine hydrochloride described already by Mignonac⁽²⁾ and Lachmann⁽³⁾.

Lastly, 1.0 gr. of benzophenone, 1.0 gr. of tetraphenylethane and 1.3 gr. of diphenyl methane were actually isolated from the residue separated from the diphenylketimine by means of hydrochloric acid.

VI. Acetonoxime.

20 gr. of the oxime and hydrogen were passed on reduced copper at 200° and 15 gr. of a liquid reaction product was obtained in a receiver cooled with a freezing mixture.

The reaction product was subjected to distillation on a water bath and the distillate boiling below 84° was collected. The distillate amounting to 12 gr. was treated with ether in an acidic solution to separate a basic from a neutral sabstance. From the ether solution, the solvent was evaporated off, and acetone was separated by means of sodium bisulphite. The yield was 3 gr.

The acid solution separated from the ether solution, was evaporated to

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(1) *Ber. D. Chem. Ges.*, 24 (1891) 3516.

(2) *Comp. rend.*, 170 (1920) 936.

(3) *J. Am. Chem. Soc.*, 46 (1924) 1477.

dryness, and by treating it with chloroform an amine hydrochloride was separated from ammonium chloride by the difference of their solubilities in the solvent.

The amine hydrochloride, amounting to 1.5 gr., was analysed after being transformed into the double salt of platinum.

0.1778 gr. subst. gave 0.0655 gr. Pt. on ignition.

Found:	Pt=36.84
Calc. for. $(C_3H_8NH_2 \cdot HCl)_2\ Pt\ Cl_4$:	Pt=36.96

From the analytical result and the carbylamine test, the basic substance was confirmed to be isopropyl amine. The occurrence of a secondary amine in the reaction product was confirmed by further reactions.

A small amount of the oxime which escaped from the reaction together with some substance of disagreeable odour and of unknown chemical nature, was isolated from the residue in a distillation flask.

January 1925.

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DETERMINATION OF THE DENSITY AND THE COMPRESSIBILITY OF ACETYLENE.

By Jitsusaburo SAMESHIMA.

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Material. The acetylene gas was prepared by the action of water on calcium carbide and then passed through tubes of copper sulphate solution, chromic acid solution, potassium hydroxide solution, solid calcium oxide and phosphorus pentoxide successively, and then frozen by liquid air.

Density of Acetylene. The density of the gas thus prepared was measured by the Dumas' method at 0°C. and 25°C. and under various pressures. The results are shown in the following table.

Temp. degree	Pressure atm.	Volume of the Dumas' bulb c.c.	Weight of acetylene gr.	Weight of one litre of acetylene gr.	Relative value of pv	
					Taking $pv=1$ at 25° and 1 atmosphere	Taking $pv=1$ at 0° and 1 atmosphere
0.00	0.5341	143.422	0.08951	0.6241		1.0053
„	0.6279	143.424	0.10539	0.7348		1.0038
„	0.9988	143.431	0.16837	1.1739		0.9995
„	1.0007	143.431	0.16852	1.1749		1.0005
„	1.5096	143.441	0.25597	1.7845		0.9938
„	1.0000	143.431	0.16849 *	1.1747*		1.0000
25.00	0.9972	143.534	0.15371	1.0709	1.0002	1.0939
„	1.0067	143.534	0.15522	1.0814	0.9998	1.0936
„	1.6391	143.546	0.25386	1.7685	0.9954	1.0888
„	1.0000	143.534	0.15416 *	1.0740*	1.0000	1.0937

* Obtained by interpolations.

The volume of the bulb was 143.4310 c.c. at 0° and 143.5338 c.c. at 25° when the pressure inside and outside were the same. The contraction of the bulb by the addition of one atmospheric pressure outside was determined by the method given in Travers' book(1), the result obtained being 0.0195 c.c. The third column of the table was calculated from these data.

The value of pv at 0°C. will be expressed by the linear equation $pv=1.0114-0.0114\,p$, for the pressure range between 0.5 and 1.5 atmospheres. If we calculate $(pv)_{p=0}$ from this equation we obtain $\frac{(pv)_{p=0}}{(pv)_{p=1}}=1.0114$.(2)

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(1) Travers, Study of Gases, London, 1901, page 119.

(2) Howarth and Burt (*Chem. Abst.* 19 (1925) 3176) obtained the value $\frac{(pv)_1-(pv)_0}{(pv)_0}=-0.00884$ or $\frac{(pv)_0}{(pv)_1}=1.00892$.

The weights of one litre of acetylene under one atmosphere are given in the table, thus 1.1747 gr. at 0° and 1.0740 gr. at 25°. The mean expansion coefficient of the gas between 0° and 25° under one atmosphere is $\frac{v_{25} - v_0}{25\, v_0} = 0.0037496$. The weight of one litre of acetylene at 0° and 1 atmosphere as determined by other authors is:

1.1712,	Leduc, *Ann. Chim. Phys.*, **15**, (1898) 36.
1.1791,	Stahrfoss, *J. Chim. Phys.*, **16**, (1918) 175.
1.1695,	Maass and Russell, *J. Am. Chem. Soc.*, **40**, (1918) 1847.

Compressibility of Acetylene. Two calibrated tubes, one of which contained acetylene and the other hydrogen, were connected with each other and dipped in a thermostat. These two gases were subjected to compression simultaneously by means of a bomb of compressed air, and the change of volume of each gas was observed. The pressure was calculated from the change in the volume of hydrogen. The following values were used for the compressibility of hydrogen.

Pressure atm.	pv at 0°C.	pv at 25°C.
1	1.0000	1.0915
5	1.0024	1.0940
10	1.0055	1.0971
15	1.0086	1.1004

The results of observations and the values calculated therefrom are summarized in the following table.

Temp. degree	Volume of gases observed		Pressure atm.	Relative value of pv	
	Hydrogen c.c.	Acetylene c.c.		Taking $pv=1$ at 25° and 1 atmosphere	Taking $pv=1$ at 0° and 1 atmosphere
0.00	2.6484	1.6756	1.000		1.0000
”	1.6062	1.0076	1.650		0.9919
”	1.4890	0.9328	1.780		0.9907
”	1.0770	0.6703	2.461		0.9846
”	1.0321	0.6418	2.568		0.9837
”	0.5935	0.3624	4.472		0.9671
”	0.3677	0.2183	7.234		0.9425
”	0.2513	0.1446	10.600		0.9148
”	0.2467	0.1415	10.798		0.9119
”	0.2366	0.1353	11.263		0.9095
25.00	2.8930	1.8309	1.000	1.0000	1.0937
”	1.2027	0.7515	2.407	0.9881	1.0808
”	0.6604	0.4064	4.389	0.9742	1.0655
”	0.3982	0.2396	7.291	0.9541	1.0436
”	0.3341	0.1989	8.697	0.9448	1.0333
”	0.2560	0.1499	11.368	0.9307	1.0180

The following values of pv have been obtained by interpolations from the above tables.

Pressure atm.	pv at 0°C.	pv at 25°C.
	(Taking $pv=1$ at 0° and 1 atm.)	
0.5	1.0057	1.0989
1.0	1.0000	1.0937
2.0	0.9891	1.0841
4.0	0.9708	1.0684
6.0	0.9530	1.0531
8.0	0.9360	1.0385
10.0	0.9194	1.0255
12.0	0.9026	1.0139

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THE RADIOACTIVE MANGANIFEROUS NODULES FROM TANOKAMI, OOMI PROVINCE.

By **Satoyasu IIMORI.**

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The feeble radioactive property of the characteristic black nodules from the bed of the Kichijo River, that runs along the Tanokami Hill, Oomi Province, has not been noticed until the author visited the locality in November, 1922. On that occasion, similar ones were also found embedded in a part of the rock body which lies just on the back of the hill side where the stream takes its rise. The nodules vary in size from about a half to two centimeters across, occurring as a pebbly constituent of the gravel-bed of the river, and are irregular in shape often with rounded edges. Some of them, often consisting, in the interior, of a mass of quartz pieces and grains of pale greenish clayey matter, are merely surrounded by a thin coating of the black material. Lying embedded in the rock which chiefly consists of coarse grains of quartz and the same clayey material as that which sometimes forms the inner parts of certain pebbly specimens, the nodules are considered to be composed of the essential black concretionary matter filling cracks of the rock.

Thin sections proved at once the black portion to be opaque and amorphous in structure, cementing abundant minute inclusions consisted of fragments of quartz and other siliceous minerals, and its secondary nature was well brought out. The mean density, determined upon six pieces containing the inclusions which amounted to about sixty per cent of the material, was found to be 2.72. Both of the specimens were brittle with a hardness of about 3 and brown black to steel grey in colour. The luster was resinous, sometimes dull and coke-like, the fracture was often fibrous or concoidal and the streak brown or black. By treatment with hydrochloric acid, the black portion of the nodule was readily and completely dissolved with evolution of chlorine, leaving a considerable residue of nearly white sandy matters, and the solution mainly gave the reactions of manganese and iron.

Analysis. In selecting material for analysis it was found practically impossible to avoid siliceous inclusions. A number of specimens of both varieties, therefore, were separately pulverized, and the portions which contained least amount of inclusions were taken for analysis; nevertheless, the insoluble gangue was present to the extent of 60 to 90 per cent as indicated in the analytical results mentioned below. Since the radioactive property was not detected in the insoluble portion, the investigation was principally directed to ascertain the composition of the soluble part. To carry out the analysis, the manganese was separated from iron and alumina by using barium carbonate in a neutral solution and by a basic acetate precipitation. The state of oxidation of manganese was determined by iodometry, that is to say, in measuring the quantity of iodine, which was liberated by the chlorine evolved by the action of hydrochloric acid upon the sample. The analytical results were as follows:

Constituents	Per cent in the pebbly nodule, found on the stream bed.		Per cent in the nodule, found on the hill side.
	(a)	(b)*	
Residue insoluble in hydrochloric acid	68.57	69.26	89.66
MnO_2	14.64	15.76	4.55
MnO	3.69	(as Mn_3O_4)	(as Mn_3O_4)
Fe_2O_3	4.66	4.70	1.20
Al_2O_3	0.78	0.83	0.82
PbO	—	—	0.40
CuO	—	—	trace
ZnO	—	—	0.31
CaO	0.74	(not looked for)	—
Ignition loss, less oxygen due to conversion of MnO_2 to Mn_3O_4	6.75	(not looked for)	2.95
Oxygen due to $MnO_2 \longrightarrow Mn_3O_4$	—	—	0.40**
	99.83		100.29

* Determined on a separately powdered portion of the same sample.

** Assuming that the ratio of MnO_2 to MnO is the same as the pebbly nodules.

In the insoluble residue of the pebbly nodule mentioned in the above table contains 55.9 per cent of silica, while 70.0 per cent of silica was found in the nodule from the hill side. The following table contains the results of the analysis recalculated excluding the insoluble part. For the purpose of comparison, some of analysis of wads given in Dana's Mineralogy(1) were quoted in the same table, together with the author's results.

Constituents	The pebbly sample	The hill-side sample	Wad	
			(A)	(B)
MnO_2	49.7	59.8	66.2	68.9
MnO	12.6		7.9	7.5
Fe_2O_3	15.8	14.6	—	2.2
Al_2O_3	2.6	9.9	—	
PbO	—	4.8	0.2	—
CuO	—	(small)		—
ZnO	—	3.7	1.6	—
CaO	2.5	—	5.0	14.4 (BaO)
H_2O	16.8	7.2	15.3	5.1
(MgO & Na_2O)	—	—	3.8	—
Total	100.0	100.0	100.0	98.1

The water was calculated from the ignition loss taking in consideration of the necessary correction for the oxidation of the manganese and the evolution of oxygen. Since the material of the rock body in which the nodules were included is practically identical with the insoluble residue previously described, similar determinations on the ignition loss were made on some pieces of the mother rock. The difference of these two determinations furnishes an approximate value of the water for the soluble part of the nodules, taking the percentage of the insoluble portion into consideration.

On the examination of the arc spectra taken by means of a quartz spectrograph, it was shown that besides the lines of the elements above described those of lead, copper, cobalt and molybdenum were detected in the soluble portion of the pebbly sample. The residue from the insoluble portion which was obtained by expelling silica by repeated evaporations with hydrofluoric acid and sulphuric acid, gave the lines of copper, tin, iron, aluminium, zinc and manganese. And in the zinc fraction of the hill-side sample, the lines of aluminium and cobalt were observed.

On the whole, it may be said that the chemical compositions of these two kinds of nodules are nearly the same and they belong to the same mineral. The analytical results, as well as the physical properties of the

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(1) E. S. Dana, System of Mineralogy, IV Edition, p. 258.

soluble portion pretty resemble with those of certain wads, except the facts that the former contains some iron oxide.

The Radium Content. Though none of radioactive constituents was chemically detected in both of the nodules, they clearly show a feeble radioactivity, when roughly examined by means of an alpha-ray electroscope. The following results, compared with the activity of uranium oxide, were obtained.

Materials examined.	Activity per gr.
Uranium oxide (as a arbitrary standard)	100.
Hokutolite from Shibukuro (for the comparison)	3.5
The pebbly sample (siliceous inclusions: 70.4%)	1.3
The hill-side sample (siliceous inclusions: 92.0%)	2.0
The insoluble residue, obtained from the pebbly sample by once extraction with HCl	0.25
Pieces of the rock, in which the nodules were found embedded . .	0.1
A mass of minute biotite flakes, collected on the bed of the Kichijo River	0.00
Pieces of a rock, stained black with the manganese oxide, collected on the river bed	0.2

Thus it appears that the radioactivity is almost concentrated in the soluble portion of the nodules, namely, in the black manganiferous matter. The activity is, however, so feeble that it needs exposures of more than three weeks in order to give the distinct effect on a photographic plate. Accordingly, there was no proper means for determining the radioactive constituents in these specimens except the measurement of the radium content. The estimation method of radium simply consisted in boiling about one gram of the powdered sample with about 4 c.c. of concentrated sulphuric acid in a test tube made of quartz glass. The emanation liberated was transferred into an emanation electroscope of the Soddy's type(1), and its effect on the rate of leak was measured in the usual way. The electroscope was standardized by using an aliquot portion of a preparation of barium-radium chloride which was previously evaluated by the γ-ray method. The constant of the electroscope, thus determined, was 24.8×10^{-12} (*i.e.* one division per minute $= 24.8 \times 10^{-12}$ gr. radium). The results obtained are given below, the activities recorded being the means of several observations.

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(1) F. Soddy, *Phil. Mag.*, [6], 18 (1909) 846.

Substances	Sample taken (gr.)	Activity (div. per min.)	Amount of Ra. (%)
The pebbly nodule	0.9139	4.24	1.15×10^{-8}
The hill-side nodule	1.3273	6.95	1.30×10^{-8}
" " "	0.9929	5.27	1.32×10^{-8}

As the whole activity is, however, attributed to the soluble part of the nodules, it follows that the amount of radium in the soluble portion of the pebbly nodule is 3.88×10^{-8} per cent, and that of the hill-side nodule 1.64×10^{-7} per cent. Thus the most remarkable character of these nodules is the fact that they contain radium in the black soluble portion, the amount of which is nearly thousand times that of the ordinary igneous rocks. The ordinary igneous rocks contain generally about 10^{-10} per cent of radium. And as might be expected, the nodules found on the river bed carries somewhat less amount of radium which is considered to have been lost probably under the action of stream water. Besides these nodules there are found in the same river bed, several rock blocks, impregnated with this radioactive secondary manganese iron oxide. This fact suggests the previous existence of primary uranium bearing minerals in this vicinity.

In conclusion, the author wishes to thank Messrs. J. Sasaki and J. Ooe for their laborious assistance in collecting the minerals, and Mr. J. Yoshimura for help in the spectroscopic examination.

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ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. I.⑴

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We know that the dielectric constants of many liquid substances have such values that their square roots (*i.e.* the refractive indices for the long electric waves) are incomparably greater than the indices of refraction for the visible and infra-red rays. These substances are, in general, chemically abnormal liquids. So if the refractive indices (n) for the electromagnetic waves of the wave lengths ranging from the order of those of visible light to

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(1) Read before the Chemical Society of Japan, January 17, 1925.

infinity be measured, we may expect that n suffers an enormous change or changes in a certain region of wave length till it attains the large value which is practically independent of wave length. Such a change (*i.e.* an anomalous dispersion) will be accompanied by an anomalous absorption, if the phenomenon be regarded as analogous to that in the case of the shorter wave lengths.

Although some authors measured the indices(1) of refraction and absorptions(2) of short electric waves, the measurements were carried out only at the ordinary temperatures and at the wave length of less than one meter. The following experiments have been undertaken to measure the anomalous dispersion and absorption at various temperatures and for various wave lengths, and to study their relations. In this first report, however, only the description of the experiment by use of the wave of 6.1 meters will be given.

The resonance method is adopted in this experiment. As a oscillation generator, a thermionic bulb is used. Fig. 1 shows the scheme of the generator circuit. H is a high-tension battery of 200 volts, F a filament battery of 6 volts, I_F an ammeter which indicates the filament current aud I_A a milliammeter in the anode circuit. H is connected in parallel with the air condenser, the capacity of which is about 1/1000 M.F. A resistance of 10000 ohms shunted by a condenser (also 1/1000 M.F.) is inserted in the grid circuit.

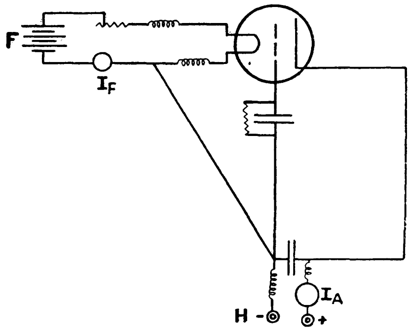

Fig. 1

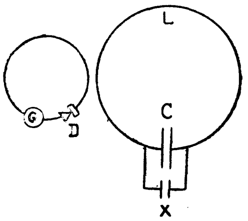

Fig. 2

The resonator consists essentially of an inductance L and the two capacities C and X as shown in Fig. 2. C is constructed from two brass bars of rectangular section (9 mm. × 5.5 mm.) placed in parallel position at a distance of 5.5 mm. Between these two, a plane-parallel glass plate is slided to vary the capacity of C. The liquid to be examined is contained in a small vessel X of about 20 c.c. with platinum wires fused in on opposite sides. The vessel X is con-

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(1) Lampa, *Wien. Ber.*, 105 (1896) 587 u. 1049.
Lang, *Wien. Ber.*, 105 (1896) 253.
Möbius, *Ann. d. Phys.*, 62 (1920) 293.
Tear, *Phys. Rev.*, II. 21 (1923) 611.

(2) Drude, *Z. physik. Chem.*, 23 (1897) 308.
Romanoff, *Ann. d. Phys.*, 69 (1922) 125.

nected in parallel with C. The detector circuit consists of a crystal detector D and a sensitive galvanometer G. All the resonating system is placed so far from the oscillator that the change of the resonating current (or the current at resonance) causes no effect upon the wave length of the oscillator.

At first the second system is adjusted to resonance to the first by sliding the glass plate of C into its suitable position, then the capacity X is filled with the liquid to be examined and the system is again brought into resonance by the same method. If the sample has no absorbing power, the resonating currents will be the same in both cases. This has been shown to be actually the case for normal organic liquids. But if the sample absorbs electric wave, for instance glycerine, the resonating current in the latter case is always considerably less than that in the former.

When the waves of a few meters were used, distilled water, acetone, benzene, the mixtures of acetone and water and those of acetone and benzene show no change of resonating current at ordinary temperatures. This is also the case when the capacity of X is changed to a considerable amount. From these results it is evident that these are non-absorbents of this wave and can be used as standard substances in the measurement of dielectric constants. In order to determine specific constants of each vessel measurements were carried out by use of these non-absorbing substances and the results show that the relation expressed by the equation (1) holds within the limit of experimental error which amounted to a few percent. The effect of reading wires from C to X which have certain small inductance are not perceptible.

$$\varepsilon-1=k\Delta C \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

ε is the dielectric constant ofthe liquid, k the specific proportional constant for the vessel, and ΔC the displacement of the glass plate from the initial position *i.e.* the position when X is filled with air only.

Merck's or Kahlbaum's reagents were used in the experiments. They were dehydrated and then subjected to fractional distillations before use.

Wave Length. If the resonating circuit is placed so far from the detector circuit that the mutual inductance is negligible, the wave length of the oscillation circuit can be calculated from the self inductance and capacity of the resonator. For this self-inductance a simple circle of copper wire were used in order that the self-inductance L can be calculated from the following formula (L–inductance, R–radious of the circle, ρ–radius of the wire used),

$$L=4\pi R(\ln R/\rho+0.079)\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

The variable capacity was calibrated, using disc condensers as the standard, the capacities of which were obtained from the following formula:

$$K=\frac{r^2}{4a}+\frac{r}{4\pi}\left(\ln\frac{16\pi r(a+d)}{a^2}+1+\frac{d}{a}\ln\frac{a+d}{d}\right)\cdots\cdots\cdots(3)$$

where K is the capacity, r the radius of the disc, d its thickness, and a the distance between two discs. Table 1 contains the observed values of wave length using various combinations of inductance and capacity. The wave length is 6.1 meters.

TABLE 1.

Inductance cm. (E.M.U.)	Capacity cm. (E.S.U.)	Wave Length m.
413	22.7	6.08
490	19.0	6.06
603	15.45	6.07
622	15.0	6.07

Mean 6.1 Meters

Dielectric Constants and Absorptions. The values of the dielectric constants and the absorptions (expressed by the change of the resonating current) at various temperatures are shown in Table 2. When the substance under examination is an absorbent, X is not a pure capacity but corresponds to a capacity shunted by a considerably low resistance. As the values of ε of such a substance were also calculated from the equivalent pure capacity, the values are only apparent in such a case. Several vessels were used to avoid the constant error characteristic to each vessel. The capacities of Vessels I, II, III are in the ratio 1 : 1.2 : 1.5.

TABLE 2.

ΔC : Displacement of the glass plate. ε : Dielectric constant.
I and I_0 : Resonating current when X is filled by the sample and by the air respectively.

Acetone.

Temp.	Vessel II.		
	ΔC	ε	$\frac{I}{I_0}$
41	3.0	18	1.0
24	3.3	20	1.0
12	3.3	20	1.0
− 3	3.5	21	1.0
−13	3.92	23	1.0
−22	4.1	25	1.0
−36	4.3	26	1.0
−49	4.7	28	1.0
−68	6.0	30	1.0
−69	6.4	32	1.0

Glycerine.

Temp.	Vessel I.			Vessel III.		
	ΔC	ε	$\frac{I}{I_0}$	ΔC	ε	$\frac{I}{I_0}$
57	4.8	36	.4	8.2	35	.2
46	5.0	37	.3	8.7	37	.2
37	5.2	39	.2	9.3	40	.08
30	5.3	40	—	9.6	41	—
24	5.4	41	.08	9.7	42	.04
20	5.2	39	.05	9.4	41	.03
18	5.1	38	—	9.2	40	—
15	5.0	38	.04	8.7	37	—
6	3.25	25	.05	5.4	24	—
− 8	1.45	12	.08	2.2	10	—
−23	0.8	7	.5	1.1	6	.2
−45	0.4	4	.9	0.7	4	—
−70	0.35	4	1.0	0.6	4	1.0

Methyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
45	28	.6	27	.4
33	29	.5	29	.4
18	32	.5	33	.2
14	—	—	—	—
10	35	.3	34	.2
0	37	.3	37	.2
− 4	—	—	—	—
− 9	39	—	39	.2
−28	44	.2	—	—
−42	49	.1	—	—
−44	—	—	—	—
−54	54	.09	—	—
−65	55	.08	—	—
−69	57	.04	—	—
−77	58	—	—	—
−84	62	.04	—	—
−89	—	—	—	—

Ethyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
63	18	.9	18	.8
53	19	.8	19	.7
45	21	—	20	—
34	22	.6	22	.5
25	24	—	23	.4
20	24	.6	23	.3
10	26	.5	25	.3
8	27	.4	26	—
− 4	28	.3	27	.2
−13	30	.2	29	.1
−18	30	.2	29	.1
−23	31	.1	—	—
−30	32	.1	31	.04
−32	31	.07	—	—
−35	—	—	32	.05
−46	31	—	30	—
−48	29	.05	29	.03
−58	22	.06	25	.03
−60	—	—	23	.03
−69	19	.05	18	.03
−71	19	.05	—	—

Propyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
60	15	.9	15	.8
50	16	.9	16	.7
45	17	.8	16	.6
36	18	.7	17	.6
26	19	.6	19	.4
23	20	.5	19	.3
16	22	—	20	.3
15	22	.4	20	—
6	—	—	21	.2
3	23	.2	21	.1
− 8	23	.2	22	.1
−20	21	.1	21	.05
−31	17	.05	17	.03
−41	13	.07	11	.05
−51	8	.1	8	.06
−59	6	.2	6	.1
−69	5	.2	5	.1

Isopropyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
55	15	.9	14	.8
45	16	.9	15	.7
37	16	.8	16	—
29	17	.7	—	—
26	19	.6	18	.4
20	19	.5	—	—
16	20	.5	20	.3
9	21	.3	—	—
3	21	.3	21	.2
− 4	21	.1	—	—
− 8	23	.1	22	.05
−16	22	.08	22	.03
−19	19	.04	—	—
−29	16	.08	17	—
−31	13	.09	—	—
−39	10	.1	—	—
−42	8	.1	9	.05
−47	7	.2	—	—
−54	5	.2	6	.1
−56	6	.2	—	—
−69	4	.4	5	.2

Butyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
59	13	.8	—	—
58	—	—	13	.7
48	14	.6	14	.5
37	16	.5	15	—
27	17	.4	16	.2
18	17	.2	18	.1
16	18	—	18	.1
13	18	—	18	—
8	19	—	19	—
7	19	—	19	.07
4	19	—	—	—
− 4	18	.06	18	.03
− 9	18	—	18	—
−15	17	.09	18	.03
−22	—	—	12	—
−29	10	.1	11	.05
−37	7	—	7	—
−47	6	.2	5	.1
−67	4	.4	4	.2

Isobutyl alcohol.

Temp.	Vessel I		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
57	13	.8	12	.8
45	14	.8	13	.6
38	15	.7	15	.6
30	16	.5	15	.3
22	16	.4	16	.2
18	17	.3	17	.1
16	18	.2	17	.1
10	18	.2	18	.09
1	18	.2	17	.09
−10	13	.1	13	.04
−19	9	.09	9	.07
−28	6	—	6	.08
−42	5	—	5	.2
−53	4	.5	4	.2
−58	4	.6	3	.4
−62	—	—	3	.6
−63	4	.7	—	—

Amyl alcohol.

Temp.	Vessel I		Vessel II		Vessel III	
	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$	ε	$\frac{I}{I_0}$
63	10.4	—	—	—	10	.7
56	—	—	11	.8	—	—
50	12	—	—	—	11	—
45	—	—	12	.6	—	—
39	13	.7	—	—	12	.5
35	—	—	13	.5	—	—
31	14	.4	—	—	14	.3
29	—	—	13	.4	—	—
24	15	.4	—	—	14	.2
20	—	—	14	.3	—	—
16	15	.2	14	.2	14	.2
14	15	.2	—	—	15	.1
9	—	—	14	.09	—	—
4	13	.1	—	—	14	.08
− 4	—	—	12	.06	—	—
−10	9	.1	—	—	9	.06
−11	—	—	9	.06	—	—
−20	7	.2	7	—	6	.08
−33	4	.3	5	.3	4	.2
−41	4	.5	3	.4	4	.3
−48	4	.5	3	.5	4	.4
−55	—	—	3	.6	—	—

Acetone. The resonating currents show no change at all temperatures. The value of ε increases as the temperature is lowered. Nothing anomalous can be found.

Glycerine. The behavior is quite different from that of acetone. Though ε changes at higher temperatures quite similarly to that of an ordinary substance, it attains a maximum value near ordinary temperature, then it decreases till it attains a value almost equal to the square of the refractive indices for visible light. As to the resonating current it decreases as the temperature is lowered, then it passes through a minimum and at last I/I_0 becomes unity. The small value of ε at the low temperature is no more an apparent one, because there is no absorption at all. Thus in this case the change of dielectric constants is quite different from that of an ordinary substance, though we are not still aware of its true value for the case in which the absorption takes place. It is evident that we are dealing here with an anomalous dispersion accompanied by an anomalous absorption as was expected.

Alcohols. Of alcohols—ethyl, propyl, isopropyl, butyl, isobutyl and amyl, the results are, in general, similar to that of glycerine. Methyl alcohol gives no maximum of apparent dielectric constants, but as there exists a considerable anomalous absorption at lower temperatures it can be expected that at still lower temperatures it will also show an anomalous change of ε.

As given above, these alcohols, monovalent as well as polyvalent, show anomalous absorptions accompanied by anomalous dispersions of the electromagnetic oscillation of the wave length of 6.1 meters. It seems that the cause of this absorption lies in the hydroxyl group contained in these compounds(1). This fact, therefore, may be used as one of the criterions to ascertain whether a compound contains this group or not. From the point of view of the classical electro-magnetic theory these substances must have their characteristic oscillations, the wave length of which corresponds to that used in this experiment. Then it should be admitted that the wave length of these characteristic oscillations varies with the temperature.

In conclusion I desire to express my best thanks to Prof. M. Katayama for his kind guidance and to Assistant Prof. D. Nukiyama for his advice on electricity.

October, 1924.

Laboratory of Physical Chemistry,
Faculty of Science, Tokyo Imperial University.

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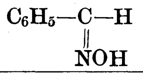
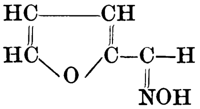
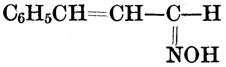
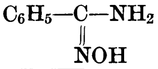
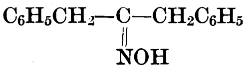
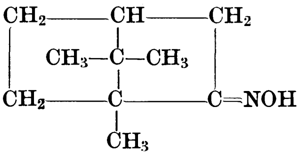
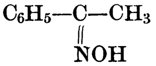
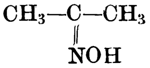
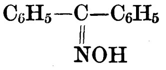
(1) Drude, *loc. cit.*

CATALYTIC ACTION OF REDUCED COPPER ON OXIMES.
(ON BECKMANN'S REARRANGEMENT. XVI.)

By Shozo YAMAGUCHI.

Received December 18, 1925. Published March 28, 1926.

Since the first report of these researches was published by the writer and Professor Komatsu(1), the present writer has described some experimental results on the same subject, which are now summarised with the present experiment in the following table :

Oxime used	Reaction product in mol %				
	$RCONH_2$	RCN	$RCOOH$	Base	$^{R}_{R'}{>}C{=}O$
1.  $C_6H_5-C(=NOH)-H$	51.9	27.5	20.6	—	—
2. 	44.6	—	trace	trace	55.4
3.  $C_6H_5CH=CH-C(=NOH)-H$	—	+	—	trace	+
4.  $C_6H_5-C(=NOH)-NH_2$	58.3	29.3	12.4	—	—
5.  $C_6H_5CH_2-C(=NOH)-CH_2C_6H_5$	11.2	12.9	11.2	—	64.7
6. 	+	+	+	trace	+
7.  $C_6H_5-C(=NOH)-CH_3$	—	+	+	+	+
8.  $CH_3-C(=NOH)-CH_3$	—	—	—	+	+
9.  $C_6H_5-C(=NOH)-C_6H_5$	—	—	—	trace	+
	Diphenyl-ketimine	Tetraphenyl-ethane		Diphenyl-methane	Ketone
	3.3	17.8		46.1	32.8

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, 6, (1923) 245; A, 7, (1925) 281; A, 9, (1925) 35.

When the oximes of different ketones or aldehydes are passed on reduced copper heated at about 200° in an atmosphere of hydrogen, as will be seen in the above table, yield acid amide ($RCONH_2$), nitrile (RCN), acid ($RCOOH$), bases ($R_2C{=}NH$, R_2CHNH_2, $(R_2CH_2)_2NH$, NH_3) ketone or aldehyde and hydrocarbons (R_2CH_2) and $(R_2CH)_2$. The yields of these compounds seem to depend more or less on the structure of the oximes ; by hydrolysis all oximes excepting benzaldoximes and benzhydroxamic acid yield principally the ketones or aldehydes from which the oximes were derived, the oximes of cinnamyl aldehyde, of acetone, of acetophenone and of benzophenone yield an acidamide of the type $RCONH_2$ as the main reaction product.

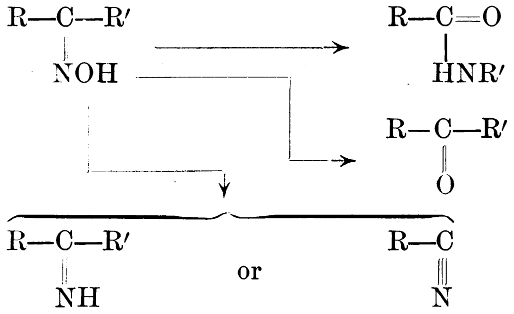
The oximes, thus, will be classified into three groups according to the chemical nature of the principal reaction products by the contact action of reduced copper at 200°.

1st. Group. The oxime of this group yields aldehyde or ketone and some basic compounds as the main reaction products, and the benzophenone and acetone oximes belong to this group. The carbonyl compound resulting by the hydrolysis of the oxime, will be transformed into hydrocarbons by the further catalytic action of reduced copper in an atmosphere of hydrogen, as actually observed in the case of benzophenone oxime.

2nd. Group. Benzaldoxime and benzhydroxamic acid each yields an acid amide which by the contact action of reduced copper, is transformed into nitrile and acid.

3rd. Group. The oxime of this group stands between the two groups of oximes above-mentioned in its behavior toward reduced copper heated at 200°, and yields the acid amide and carbonyl compounds with some basic ones. Their relative amount in the reaction product depending more or less upon the chemical or electronical nature of the hydrocarbon radicals linked to the carbon atom of the methane nucleus of the oxime. Furfuraldoxime, cinnamylaldoxime, dibenzylketoxime, camphoroxime and acetophenone oxime belong to this group.

As a matter of fact, aldoximes and ketoximes or their salts, probably suffer the chemical reactions from heat, being transformed directly ; (1) into its isomeric acid amides—Beckmann's rearrangement ; (2) into carbonyl compounds—aldehyde or ketone by hydrolysis ; (3) into imine or nitrile by dehydration and the latter substance will also result from an acid amide :



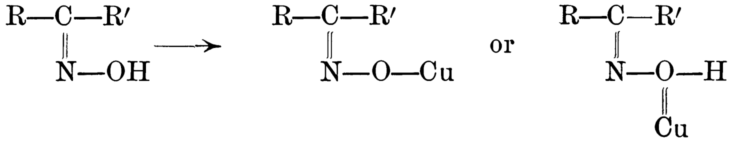
$$\underset{\substack{|\\ \text{NOH}}}{\text{R—C—R}'} \longrightarrow \underset{\substack{|\\ \text{HNR}'}}{\text{R—C=O}} \qquad (1)$$

$$\longrightarrow \underset{\substack{\|\\ \text{O}}}{\text{R—C—R}'} \qquad (2)$$

$$\underset{\substack{\|\\ \text{NH}}}{\text{R—C—R}'} \quad \text{or} \quad \underset{\substack{\|\|\\ \text{N}}}{\text{R—C}} \qquad (3)$$

Such direct transformations of the oximes or their salts by heat would take place independently or simultaneously according to the chemical nature of the oximes. In presence of reduced copper, the velocity of these reactions will also evidently be modified, some reactions being accelerated and others retarded, and as a consequence, the oxime, from the view point of the nature of chemical reactions, were classified into the three groups mentioned above.

With regard to the catalytic action of reduced copper on the behavior of the oxime toward heat, the writer has attempted to explain its mechanism with the following interpretations. When an oxime is passed in a vapour state over finely divided copper, it would be condensed in a thin layer on the surface of the catalyst, and temporarily form a compound—a salt or an oxonium compound,—though its combination is in a labile state.



$$\underset{\substack{\|\\ \text{N—OH}}}{\text{R—C—R}'} \longrightarrow \underset{\substack{\|\\ \text{N—O—Cu}}}{\text{R—C—R}'} \quad \text{or} \quad \underset{\substack{\|\\ \text{N—O—H}\\ \|\\ \text{Cu}}}{\text{R—C—R}'} \qquad (4)$$

Moreover, in the present case, an hypothetical substance of the composition CuH_2 should occur in the reaction system, since hydrogen is spread uniformly in the reaction system. The dissociation of these compounds will take place, in the course of evaporation, on the surface of the metal, and where the chemical transformations mentioned above take place. During the evaporation of the oxonium compound on the surface of the catalyst, the combining force between the hydrocarbon radicals and the carbon atom of the methane nucleus of the oxime is smaller than that between the nitrogen and the carbon atoms. Moreover, when the metal combined with the oxime behaves to lose the strength of the former affinity by acting as a donor of electrons, as sodium does in the molecular rearrangement of the oxime observed by S. Komatsu and T. Hiraidzumi(1). The molecular rearrangement of the oxime into its isomeric acid amide will take place with a prominent yield, but in the meantime, the hydrocarbon radical detached by the influence of

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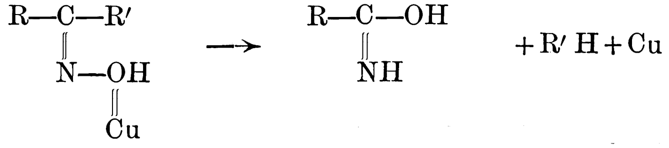
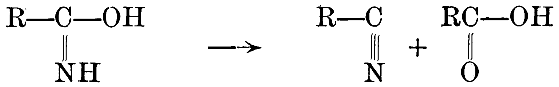
(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, 8, (1925) 273.

the catalyst, is left in a free state without entering into combination with the nitrogen atom, and as a consequence the simple acid amide of the formula $RCONH_2$ results, and this by the further action of the catalyst is soon transformed partly into nitrile and acid, which may be represented by the following scheme :



$$\begin{array}{c}R-C-R'\\ \| \\ N-OH\\ \| \\ Cu\end{array} \longrightarrow \begin{array}{c}R-C-OH\\ \| \\ NH\end{array} + R'H + Cu \qquad (5)$$

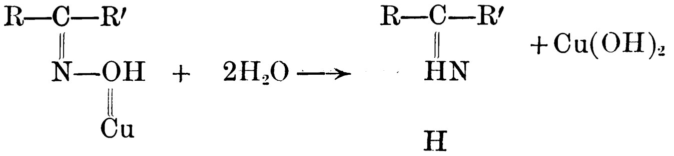


$$\begin{array}{c}R-C-OH\\ \| \\ NH\end{array} \longrightarrow \begin{array}{c}R-C\\ \equiv \\ N\end{array} + \begin{array}{c}RC-OH\\ \| \\ O\end{array} \qquad (6)$$

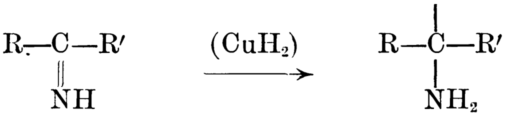
The transformation of the second group of oximes into acid amide, nitrile and acid by the contact action of the catalyst, will be represented by the schemes (1) and (6).

When however, the linkings between the hydrocarbon radicals or the hydrogen and the carbon atom of the methane nucleus of the oxime are quite strong, and the metal exerts no appreciable influence on these affinities, the hydrolysis will results in the formation of an aldehyde or a ketone, one part of which will be reduced into hydrocarbon, by the catalytic action of reduced copper in an atmosphere of hydrogen as noticed in the case of the benzophenone oxime. The hypothesis would be applied to the explanation of the reactions of the first group of oximes.

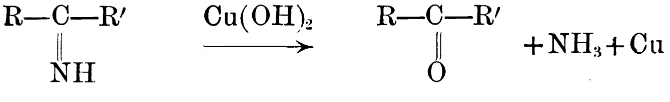
If the dissociation of the linking between the hydroxyl group and the nitrogen atom, by heat or by the catalytic influence of reduced copper, takes place very easily, then the formation of imine or nitrile will occur and the conversion of the imine into base or ketone by catalytic reduction or hydrolysis in presence of the catalyst will take place in turn :



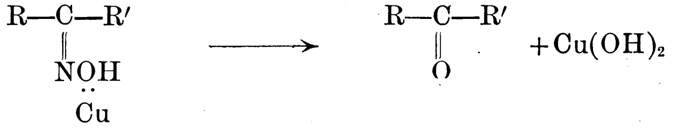
$$\begin{array}{c}R-C-R'\\ \| \\ N-OH\\ \| \\ Cu\end{array} + 2H_2O \longrightarrow \begin{array}{c}R-C-R'\\ \| \\ HN\end{array} + Cu(OH)_2 \qquad (7)$$



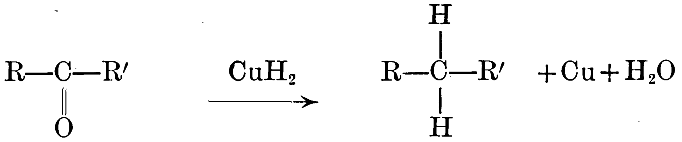
$$\begin{array}{c}R-C-R'\\ \| \\ NH\end{array} \xrightarrow{(CuH_2)} \begin{array}{c}H\\ | \\ R-C-R'\\ | \\ NH_2\end{array}$$



$$\begin{array}{c}R-C-R'\\ \| \\ NH\end{array} \xrightarrow{Cu(OH)_2} \begin{array}{c}R-C-R'\\ \| \\ O\end{array} + NH_3 + Cu \qquad (8)$$



$$\underset{\substack{\| \\ \mathrm{NOH} \\ \cdot\cdot \\ \mathrm{Cu}}}{\mathrm{R{-}C{-}R'}} \longrightarrow \underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R{-}C{-}R'}} + \mathrm{Cu(OH)_2} \qquad (9)$$



$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R{-}C{-}R'}} \xrightarrow{\mathrm{CuH_2}} \underset{\substack{| \\ \mathrm{H}}}{\overset{\substack{\mathrm{H} \\ |}}{\mathrm{R{-}C{-}R'}}} + \mathrm{Cu} + \mathrm{H_2O} \qquad (10)$$

The behavior of the oximes of the first group, by the contact action of reduced copper will be represented in schemes (7) (8) and (10).

As was mentioned in the previous article,(1) the chemical reactions of the oximes will depend more or less upon the chemical and electronical nature of the hydrocarbon radicals, or in other words, the mobility of the radicals from the carbon atom of the methane nucleus depending mostly upon their electronical character, and also upon the catalytic influence of the catalyst presented in the reaction system, and all of the reactions shown in the schemes (1) (7) (8) and (10) would take place of some oximes belonging to the 3rd. group, possessing the chemical characters of both groups, in some degree. The conception of these ideas with respect to the conversion of the oxime into the acid amide, the carbonyl compound, and bases was thus fully illustrated by the experimental results mentioned in the above table.

January 1925.
Laboratory of Organic and Bio-Chemistry,
College of Science, Kyoto Imperial University.

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(1) S. Komatsu and T. Hiraidzumi, *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, **8**, (1925) 273.

THE VAPOUR PRESSURES OF HYDROGEN CYANIDE⁽¹⁾

By Heima SINOZAKI, Ryozaburo HARA, and
Shinroku MITSUKURI.

Received March 12, 1926. Published April 28, 1926.

The vapour pressures of hydrogen cyanide were measured at various temperatures between 0°—46° by two of the present authors⁽²⁾, and, between −15°—183°, by Bredig and Teichmann⁽³⁾. In the present experiments, the vapour pressures at the low temperatures below zero degree centigrade were measured and the experimental equations for the vapour pressures of solid and liquid hydrogen cyanide were obtained.

The pure hydrogen cyanide obtained in the same way as in the previous experiment⁽⁴⁾ was twice fractionally distilled with the aid of solid carbon dioxide and liquid air in the closed system, which had been previously evacuated perfectly; and the final distillate was again distilled into the measuring bulb. The bulb was placed in the thermostat whose temperature was automatically regulated constant within 1/100 degree⁽⁵⁾. A closed type manometer was connected to the bulb and the difference of the mercury levels was measured with a cathetometer made by the Société Genevoise.

The results were tabulated in the tables 1 and 2, of which the former was relating to the liquid and the latter to the solid. In both of them, the second columns give the absolute temperatures measured by a platinum thermometer, and the third columns, the observed vapour pressures, each of which is the mean of the several independent observations at the same temperature. These values of the pressures are given in the height of the mercury at 0°, reduced to the sea level at 45° latitude.

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(1) This paper is an abstract from the original one, which was read before the monthly meeting of the Chemical Society of Japan in Tokyo on March 6th., 1926, and which is to be published in the Journal of the Chemical Society of Japan (in Japanese) and the Technology Reports of the Tohoku Imperial University (in English).

(2) Hara and Sinozaki, *J. Soc. Chem. Indust. Japan*, 26 (1923), 884. *Technology Reports, Tohoku Imperial University*, IV, (1924), 145.

(3) Bredig and Teichmann, *Z. Electrochem.* 31 (1925), 449.

(4) Hara and Sinozaki, loc. cit.

(5) Sinozaki and Hara, *J. Soc. Chem. Indust. Japan*, 29 (1926).

TABLE 1.

Exp. No.	T° abs.	P obs. mm.	Pcalc. (1) mm.	Pcalc.(1) $-P$obs. mm.	Pcalc. (2) mm.	Pcalc.(2) $-P$obs. mm.	Pcalc. (3) mm.	Pcalc.(3) $-P$obs. mm.
29′	256.74	120.05	120.92	+0.87	118.40	− 1.65	119.84	−0.21
5′	259.92	140.78	141.90	+1.12	140.00	− 0.78	141.16	+0.38
28′	260.07	142.32	142.92	+0.60	141.08	− 1.24	142.23	−0.09
26′	261.12	149.80	150.57	+0.77	148.81	− 1.76	149.85	+0.05
27′	262.12	157.58	158.16	+0.48	156.41	− 1.75	157.36	−0.22
4′	262.85	163.16	163.95	+0.79	162.24	− 0.92	163.10	−0.06
3′	265.63	186.51	187.36	+0.82	185.98	− 0.56	186.50	−0.04
2′	268.96	219.81	219.08	−0.73	218.14	− 1.67	218.21	−1.6
1′	272.40	256.31	256.47	+0.16	256.02	− 0.29	255.54	−0.77
16	273.18	265.2	265.7	+0.5	265.33	+ 0.1	264.73	−0.5
1	277.19	316.8	317.3	+0.5	314.86	− 1.9	316.34	−0.5
2	280.07	358.6	359.3	+0.7	360.15	+ 1.6	358.34	−0.3
3	283.09	407.8	408.2	+0.4	409.59	+ 1.8	407.28	−0.5
4	286.27	465.4	465.5	+0.1	467.44	+ 2.0	464.66	−0.7
5	288.98	519.4	519.4	—	521.79	+ 2.4	518.67	−0.7
6	291.97	584.7	584.6	−0.1	588.72	+ 4.0	584.17	−0.5
7	294.90	654.4	655.0	+0.6	658.17	+ 3.8	654.82	−0.4
8	297.75	730.6	730.1	−0.5	733.27	+ 2.7	730.10	−0.5
9	300.78	816.2	817.7	+1.5	820.37	+ 4.2	817.75	+1.6
10	303.75	911.1	911.2	+0.1	913.48	+ 2.4	911.84	+0.7
11	307.08	1028.4	1026.6	−1.8	1027.5	− 0.9	1027.6	−0.8
12	309.78	1128.2	1128.2	—	1127.9	− 0.3	1130.0	+1.8
13	313.25	1272.2	1271.1	−1.1	1268.0	− 4.2	1273.5	+1.3
14	316.02	1393.2	1395.5	+2.3	1389.2	− 4.0	1398.4	+5.2
15	319.39	1564.1	1559.2	−4.9	1548.3	−15.8	1563.4	−0.7

TABLE 2.

Exp. No.	T° abs.	Pobs. mm.	Pcalc. (5) mm.	Pcalc. (5)$-P$obs. mm.	Pcalc. (6) mm.	Pcalc. (6)$-P$obs. mm.
21′	187.09	0.132	0.143	+ 0.011	0.161	+ 0.029
20′	194.52	0.376	0.382	+ 0.006	0.411	+ 0.035
19′	199.76	0.745	0.729	− 0.016	0.733	− 0.012
18′	206.44	1.562	1.564	+ 0.002	1.602	+ 0.04
17′	207.11	1.673	1.685	+ 0.012	1.720	+ 0.047
16′	212.41	2.97	2.95	− 0.02	2.98	+ 0.01
15′	217.52	4.97	4.93	− 0.04	4.93	− 0.04
14′	221.84	7.48	7.43	− 0.05	7.39	− 0.09
13′	227.00	11.78	11.85	+ 0.07	11.75	− 0.03
12′	229.02	13.92	14.13	+ 0.21	14.00	+ 0.08
11′	233.13	19.72	19.99	+ 0.27	19.79	+ 0.07
10′	238.87	31.24	31.69	+ 0.45	31.42	+ 0.18
9′	243.96	46.26	46.71	+ 0.45	46.43	+ 0.17
8′	248.78	66.03	66.34	− 0.31	66.13	+ 0.10
7′	254.02	96.26	95.33	− 0.93	95.53	− 0.73
30′	254.46	97.97	96.27	− 1.70	98.45	+ 0.48
22′	258.83	131.29	130.99	− 0.36	131.97	+ 0.68
6′	258.87	131.93	131.26	− 0.67	132.35	+ 0.42
23′	259.18	134.29	133.98	− 0.31	135.03	+ 0.74
24′	259.56	137.45	137.30	− 0.15	138.53	+ 1.08

From the values of the above tables, the following experimental equations were obtained, in which (1) to (4) were those for liquid, and (5) and (6) were those for solid.

$$\log P_{\text{mm.}} = \frac{-1836.63}{T^{1.05}} + 7.5030 \quad \cdots\cdots\cdots(1)$$

$$\log P_{\text{mm.}} = \frac{-1556.14}{T} + 1.75 \log T - 0.0038273\, T + 4.90192 \quad \cdots\cdots(2)$$

$$\log P_{\text{mm.}} = \frac{-1460.04}{T} + 0.47647 \log T - 0.0007344\, T + 6.82130 \quad \cdots\cdots(3)$$

$$\log P_{\text{mm.}} = \frac{-1732.58}{T} + 1.75 \log T - 0.010760\, T + 8.3163 \times 10^{-6}\, T^2 + 6.82130 \quad \cdots\cdots(4)$$

$$\log P_{\text{mm.}} = \frac{-9745.56}{T^{1.35}} + 7.5030 \quad \cdots\cdots\cdots(5)$$

$$\log P_{\text{mm.}} = \frac{-2014.39}{T} + 1.75 \log T - 0.004077\, T + 6.82130 \quad \cdots\cdots(6)$$

The equations (1) and (5) are those of Henglein type⁽¹⁾, and the values calculated by those equations and the differences from the observed values are given in the fourth and the fifth columns of both tables.

The equations (2) and (6) are those of Nernst type. The values calculated with the equation (6) are given in the sixth column in the table 2, which coincide with those observed as indicated in the seventh column of the same table. But the values calculated with the equation (2) for the vapour pressure of the liquid do not coincide with those observed. The present authors, therefore, modified the equation (2) as (3) and (4), of which the equation (3) was obtained by the least square method from the observed values, the last term being taken as the same as that in the equation (6), and the equation (4) was obtained also by the least square method, whose second and the last terms being taken as constant. Of these two equations, the former gives the best calculated values for the liquid as indicated in the 8th and 9th columns of the table 1, and the latter gives only a little better values than those from the equation (2).

The full details of the experiments and some thermodynamical calculations are to be found in the original paper.

February 28, 1926.

The Chemical Technological Institute,
Engineering College, Tohoku Imperial University,
Sendai.

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(1) Henglein, *Z. physik. Chem.*, 98 (1921), 1.

ON THE CRYSTAL STRUCTURE OF PENTA-ERYTHRITOL.

By Isamu NITTA.

Received March 13, 1926. Published April 28, 1926.

The presence of a non-tetrahedral carbon atom in the crystal of penta-erythritol, $C(CH_2OH)_4$, has been reported by H. Mark and K. Weissenberg⁽¹⁾ and recently by M. L. Huggins and S. B. Hendricks⁽²⁾. Now that there is no other X-ray investigation yet imparted which confirms the presence of such carbon atom in organic crystals, while the theory of the tetrahedral carbon atom has actually offered a great deal of applications to organic chemistry, it seems not insignificant to reexamine if there can never be a possibility of attributing the tetrahedral nature to the central carbon atom of penta-erythritol in crystalline state. Thus the reexamination was carried out using the Laue photographic and X-ray spectrometric methods. Mark and Weissenberg used the rotating crystal method, and their results will be summarized as follows. The unit cell, containing two chemical molecules, has the dimensions $a=6.16$ Å. and $c=8.76$ Å., and the corresponding space group is C_{4v}^9, the underlying translation lattice being tetragonal body centred. The symmetry of the molecule and of the central carbon atom is that of the point group C_4^v, the four substitution radicals CH_2OH are structurally equivalent and lie on the hemimorphic reflection planes. Huggins and Hendricks reported that they came also at the same results.

Penta-erythritol from Kahlbaum was recrystallized from aqueous solution and used in the investigation. The symmetrical Laue photograph, obtained with the incident X-ray beam normal to the cleavage plane (001), showed a simple tetragonal pattern indicating the absence of the planes of symmetry parallel to the tetragonal axis, quite similar to the case of iodoform⁽³⁾, Thus it is evident that the space group C_{4v}^9 already reported is not a correct one for the crystal of penta-erythritol, for the symmetry class C_4^v possesses the planes of symmetry parallel to the tetragonal axis. The space groups conformable to the Laue photographic indications should be those which belong to the point groups S_4, C_4 and C_4^h. Besides the Laue photograph, several reflections from various atomic planes were investigated with an X-ray spectrometer. The dimensions of the unit cell and the kind of the underlying translations agree altogether with those determined by Mark and Weissenberg.

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(1) H. Mark and K. Weissenberg, *Z. Physik.* 17 (1923), 301.

(2) M. L. Huggins and S. B. Hendricks, *J. Am. Chem. Soc.*, 48 (1926), 164.

(3) I. Nitta, *Scientific Papers of the Institute of Physical and Chemical Research*, 4 (1926), 49.

From these Laue photographic and X-ray spectrometric data the possible space groups are limited to S_4^2, C_4^5, C_4^6, C_{4h}^5 and C_{4h}^6. In order to sort out the corresponding space group, it is necessary to take into consideration the arrangement of the atoms in the unit cell; i.e. the arrangement of 10 carbon atoms, 24 hydrogen atoms and 8 oxygen atoms. From the space groups C_{4h}^5 and C_{4h}^6 there can be deduced no arrangement that accounts for the observed reflections from (001) plane, and in the case of C_4^6 we cannot arrange 10 carbon atoms conformably in the unit. Only two space groups S_4^2 and C_4^5 remain as the possible ones. Theoretically these two can be distinguished by the observation of the reflections from (001) plane, and the obtained data are somewhat favourable to S_4^2. As the problem hangs upon this point, these data may not be sufficient to decide S_4^2 as the correct one and the trial survey upon the atomic arrangements will be needed for each of the two groups. It is tedious indeed to carry this work through, for, although the parameters governing 24 hydrogen atoms are neglected, there are still six parameters to be determined. In this note it will, therefore, be discussed only what inference can be made for each of the alternatives.

In either case of S_4^2 and C_4^5 we can arrange four structurally equivalent alcohol radicals CH_2OH around the central carbon atom. The minimum possible symmetry of the molecule is that of the point group S_4 in the case of S_4^2, while it is C_4 in C_4^5. It implies that we are dealing with the tetrahedral central carbon atom in the former case and the non-tetrahedral one in the latter. This possibility of the tetrahedral nature of the cental carbon atom, which the observed reflections from (001) plane seem to favour, is what the above mentioned authors have not adverted to, and what will be of some importance from the chemical point of view. The determination of the parameters is now going on; and the full account will be published later as one of the Scientific Papers of the Institute of Physical and Chemical Research.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.

CATALYTIC ACTION OF REDUCED COPPER ON PINACONES.

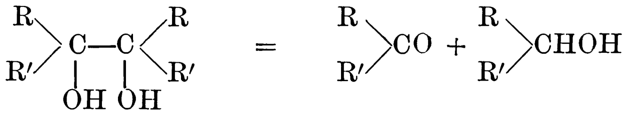
By Shozo YAMAGUCHI.

Received February 3, 1926. Published April 28, 1926.

In the recent articles(1) on the catalytic action of reduced copper on oximes, it was already stated by the present writer that reduced copper heated at 200° acts on the oximes to promote, on the one hand, reduction like reduced nickel, and on the other, Beckmann's rearrangement, and the latter action was noticed to be similar to that of dilute sulphuric acid on oximes.

Hence, it may naturally be anticipated that the reduced copper is also capable, under certain conditions, of exercising a catalytic influence on the transformation of pinacones into pinacolines, which was actually observed by many investigators in the case of the action of dilute sulphuric acid on pinacones.

According to W. Thorner and Th. Zincke(2), the pinacones derived from benzophenone and acetophenone, when heated above their melting points (280°–300°), decomposed completely into the corresponding ketone and alcohol, as is shown in the following scheme :



It seems, therefore, an interesting problem from the view point of the contact action, to see what chemical change would take place when these pinacones come into contact with reduced copper heated at about 200°. The present experiment was undertaken to study the catalytic action of this metal and moreover to obtain some facts which might throw some light upon the mechanism of the pinacoline transformation.

1. **Benzophenon-pinacone.** The pinacone of m.p. of 168°–169°, which was prepared from benzophenone by reduction with zinc and sulphuric acid in an alcohol solution, according to the directions of Ed. Linnemann,(3) and W. Thorner and Th. Zincke(4), was passed on reduced copper heated at 200°. The reaction products remained almost entirely on the catalyst, due to their non-volatility, was treated with chloroform and separated from the catalyst by filtration. The product, thus obtained, amounted to 8 gr. (from 10 gr. of the

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(1) This journal, 1 (1926), 35 and 54.

(2) *Ber.*, 13 (1880), 641.

(3) *Lieb. Ann.*, 133 (1865), 26.

(4) *Ber*, 10 (1877), 1473.

pinacone), and was ascertained to be composed of 7 gr. of pure benzophenone pinacoline with a m.p. of 177°–179°, after being purified by the method suggested by C. Paar(1). On analysis, it gave the following results :

0.1122 gr. subst. gave 0.3674 gr. CO_2 and 0,0576 gr. H_2O. (Found : $C=89.30$; $H=5.74$. $C_{26}H_{20}O$ requires $C=89.63$; $H=5.77\%$).

For confirmation, 4 gr. of the pinacoline have converted, by hydrolysis with an alkali solution, into 3 gr. of pure triphenyl methane (m.p. 92°–93°) and 1.0 gr. of pure benzoic acid (m.p. 121°), and both substances were confirmed by the determination of the chemical and physical properties and also by the elementary analyses :

0.1135 gr. of the hydrocarbon gave 0.3867 gr. CO_2 and 0.0687 gr. H_2O. (Found : $C=92,92$; $H=6.77$. $C_{19}H_{16}$ requires $C=93.42$; $H=6.58\%$). 0.1099 gr. of the acid gave 0.2773 gr. CO_2 and 0.0502 gr. H_2O. (Found : $C=68.70$; $H=5.11$. $C_7H_6O_2$ requires $C=68.84$; $H=4.92\%$).

Thus, the pinacoline which was obtained by the contact action of reduced copper on benzophenone pinacone, was confirmed to be the same substance which was previously obtained by other chemists(2) from the same pinacone by means of acetyl chloride, benzyl chloride, dilute sulphuric acid, oxalic acid and concentrated hydrochloric acid heated above 200°.

2. **Acetophenone-pinacone.** Applying the contact action of reduced copper at 130°–140° on 13 gr. of acetophenone-pinacone, m.p. 120°, prepared from acetophenone(3), 6.6 gr. of liquid and 4 gr. of solid reaction products were obtained.

The liquid reaction product consisted, on distillation, of the following fractions :

140°–160°, trace ; 160°–205°, 3.0 gr. ; Residue, 2.4 gr.

The second fraction was confirmed to consist mainly of acetophenone by oximiration with hydroxylamine, and the residue as well as the solid reaction product above mentioned were noticed to be composed mostly of the pinacone (m.p. 120°) unchanged in the reaction.

In the second reaction of the pinacone carried out at higher temperature such as 180° and 200°, no other chemical reaction than that mentioned above, could be observed.

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(1) *Ber.*, **17** (1884), 911.

(2) W. Thorner and Th. Zincke, loc. cit.
C. Paar, Loc. Cit.
E. Erlenmeyer, *Ber.*, **14** (1881), 322.
U. Nef, *Lieb. Ann.*, **318** (1901), 37 ; **335** (1904), 243.
H. Meerwein, *Lieb. Ann.*, **376** (1910), 152; **396** (1913), 200; **405** (1914), 129; **417** (1918), 225; **419** (1919), 121.
F. Henrich, "Theorien der Organischen Chemie," 5 Auflage (1924) p. 444."

(3) *Ber.*, **10** (1877), 1714.

Such a difference in the behavior of the pinacones toward reduced copper heated at about 200°, would be ascribed either to the chemical affinity between two tertiary carbons of the pinacone molecule or to some other reason, and further experiments are required to discover an explanation which will cover the facts underlying the pinacoline transformation, one of the most interesting problems in modern organic chemistry.

September 1925.
Laboratory of Organic and Bio-chemistry.
College of Science, Kyoto Imperial University.

ACTION DE L'AMIDURE DE SODIUM SUR DES COMPOSÉS ORGANIQUES.⑴

Par **Itizo KASIWAGI.**

Reçu le 27 février 1926. Publié le 28 avril, 1926.

I. L'amidure de sodium sur le benzile.⑵ Quand on chauffe un mélange des solutions, qui est formé en ajoutant une molécule de benzile dissout dans toluène sec sur une molécule d'amidure de sodium bien pulverisé couvert par le même dissolvant, la réaction se produit entre ces deux corps. On poursuit le chauffage pendant plusieurs heures. On ajoute ensuite de l'eau dans le mélange et sépare la portion aqueuse, que l'on acidifie, pour faire precipiter l'acide benzilique. De la portion toluénique on recouvre une quantité plus ou moins grande de benzile échappé à la réaction selon la durée de chauffage. L'identification de cet acide se fait par son point de fusion et par la coloration caractéristique de ce corps avec H_2SO_4 conc. Le rendement en ést presque quantitatif.

L'amidure de sodium agit sur le benzile similairement que l'on traite le dernier avec de l'alcali caustique.

II. Le même réactif sur le furfural. Par une manipulation semblable à I, on obtient avec deux molécules de furfural et deux molécules d'amidure de sodium, une molécule d'acide pyromucique et un peu moins d'une molécule d'alcool furfurylique. La réfraction moléculaire de cet alcool donne une

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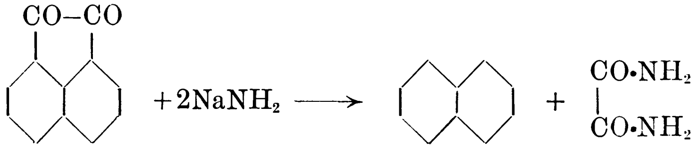
(1) Les rapports des expériences furent brûlés par l'incendie du premier septembre 1923, le jour du grand tremblement de terre. Les travaux I et III se faisaient au laboratoire de M. A. Haller. professeur regretté de l'Université de Paris, à qui je tiens à exprimer ici ma reconnaissance.

(2) A. Haller, *Conference*; *Bull. Soc. Chim.*, [4], 31 (1922), 1141.

valeur très voisine de celle donnée par Gennari(1). Son point d'ébullition coincide avec celui de l'alcool. L'identification de l'acide pyromucique se fait par son point de fusion et sa propriété d'être sublimable.

Parallèlement on a étudié la réaction entre le benzylal et l'amidure de sodium, et on a obtenu le benzylol et l'acide benzoique par le même traitement. Cette dernière réaction était déjà étudiée(2), et on obtenait l'alcool et le *benzamide*. Le but de notre travail est l'obtention de *l'acide benzoique* même au lieu du benzamide.

III Le même sur l'acénaphtène. L'amidure de sodium ne réagit pas sur l'acénaphtène dans le milieu toluénique, même quand on fait élever la température jusqu'au point d'ébullition du dissolvant. On chauffe avec soin le mélange de ces deux substances à l'état de poudres fines, et la réaction a lieu brusquement environ à 80°, en dégageant une fumée brune et dense, qui monte jusqu'à l'extrémité du tuyau qui s'attache au ballon. Le produit dans le ballon et dans le tuyau a l'odeur très forte caractéristique du naphtaléne. La rèaction peut s'exprimer probablement :



Ce travail est à suivre.

Haute école polytechnique de Yokohama.

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(1) Gennari, *Gazz. chim. ital.*, **24**, I (1894), 247.

(2) Haller et Bauer, *Ann. Chim.*, **16** (1909), 152.

ON THE CATALYTIC HYDROGENATION OF THE CARBONYL GROUP IN AROMATIC COMPOUNDS UNDER PRESSURE IN THE PRESENCE OF COPPER. PART II.

By **Bennosuke KUBOTA** and **Taro HAYASHI.**

Received March 4, 1926. Published April 28, 1926.

In the previous communication(3) it was published that copper is a suitable catalyst for hydrogenation of carbonyl group in aromatic compounds under pressure in order to get alcohols, and the experiments with diketones were shown. In this paper we describe the experiments with monoketones.

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(3) B. Kubota and T. Hayashi, This journal, 1 (1926), 14.

1. **Acetophenone $C_6H_5{\cdot}CO{\cdot}CH_3$.** This was treated at 140° (the temperature of the oil bath) under 66 atmospheric pressure (initial) as was described in Part I⑴, and a viscous liquid was obtained. It was fractionated under 12 mm. pressure and the following fractions were collected : 80–88°, 88–89° (4%) and 89–92° (very little). The first fraction was found to be unchanged acetophenone forming semicarbazone which melts at 185–186°. The second fraction was warmed with phenyl isocyanate for a few hours on the water bath and allowed to stand over night. The crystalline mass separating out was recrystallised by means of a mixture of alcohol and petroleum ether. It separated out in white crystals melting at 92° and its properties were found to be in good agreement with those of methyl phenyl carbinol of Klages⑵.

Acetophenone was next treated at 160° under 66 atmospheric pressure. The product consisted of a mixture of a colourless liquid and crystals. The whole mass was fractionated under 15 mm. pressure and the following fractions were collected : 33–34°, 95–96° and residue.

The first fraction was a colourless liquid which distilled at 136–137° under ordinary pressure, and was identified as ethyl benzene. The second fraction proved to be nothing but unchanged acetophenone forming semicarbazone which melts at 185–186°. The residue solidified when cooled and being recrystallised with a mixture of alcohol and petroleum ether, it separated out in needles. It melted with partial sublimation at 123–124° and was, no doubt, dimethyl diphenyl ethane.⑶

2. **Benzophenone. $C_6H_5{\cdot}CO{\cdot}C_6H_5$.** This was treated at 120° under 50 atmospheric pressure. The product consisted of colourless crystals with orange-like smell (about 98%) and very small quantities of colourless viscous liquid. The crystals being recrystallised with alcohol were found to melt at 67–67.5° and to possess the properties of diphenyl carbinol, whose benzoic acid ester melting at 82–83° is formed by the fusion with benzoic acid, and whose colour reaction by fuming nitric acid shows blood red and so forth. The liquid product solidified on being cooled with a freezing mixture and melted at 26°, which proved beyond doubt that it was diphenyl methane.

Benzophenone was next treated at 190° under 52 atmospheric pressure. It resulted in a viscous liquid with a good smell (92%) and some crystals. The liquid was subjected to distillation, producing a distillate which boils at 185–212° under 65 mm. pressure and white crystals which remained in the flask. The distillate, crystallising on being cooled in small needles which melt at 26°, proved to be diphenyl methane as described above. The crystals which remained in the frask were recrystallised with alcohol and its pro-

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(1) B. Kubota and T. Hayashi, loc. cit.

(2) Klages and Allendorf, *Ber.*, **31** (1898), 1003.

(3) Engler u. Berthge, *Ber.*. **7** (1874), 1127.

perties were found to be in good agreement with those of tetraphenyl ethane of Zincke.(1)

3. **Camphor $C_{10}H_{16}O$.** Camphor (melting at 176–176.5°, $[\alpha]_D^{15} = +44.51°$) was treated at 120–150° for 12–50 hours under 10–92 atmospheric pressure (initial). The melting points and the compositions calculated from their rotatory power are represented as follows :(2)

Inital pressure of hydrogen.	Duration of the reaction.	Temperature of the oil bath.	Melting point of the product.	$[\alpha]_D$ of the product.	Composition	
					Isoborneol (%)	Borneol (%)
(atm.) 30	(hour.) 13.4	150	207.5-208.5°	−18.16°	78.8	21.2
10	12	140	204 -206°	−16.53	76.4	23.6
65-92	50	120	204 -205.5°	−12.26	70.9	29.1

The composition was calculated from the following formula given by Beckmann,(3)

$$\alpha = \frac{\alpha_1 m_1 + \alpha_2 m_2}{m_1 + m_2}, \qquad m_1 = \frac{\alpha - \alpha_2}{\alpha_1 - \alpha_2} \times 100,$$

where, α denotes the value of $[\alpha]_D$ of the product,

α_1 „ „ „ „ $[\alpha]_D$ of L-isoborneol = −33°,

α_2 „ „ „ „ $[\alpha]_D$ of R-borneol = +37°,

m_1 denotes the percentage of L-isoborneol,

m_2 „ „ „ „ R-borneol.

Hulett(4) showed that the effect of the pressure on the melting point of camphor was to be represented by the formula $\frac{dt}{dp} = 0.1290$, up to the pressue of 300 atmospheres. The melting points observed by him between 50 and 175 atmospheres are as follows :

Pressure in atm.	Melting point	Pressure in atm.	Melting point
50	183.7°	125	193.7°
75	187.5	150	197.0
100	190.5	175	200.4

Thus it is clear that the temperature from 120° to 150°, as in the case of our experiments, are not sufficiently high to melt the camphor under the

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(1) Zincke, *Ann.*, 159 (1871), 374.

(2) These results were obtained by the observations of Mr. Ikuo Midzuno.

(3) Beckmann, *J. prakt. Chem.*, 55 (1897), 34.

(4) Hulett, *Z. physik. Chem.* 28 (1899), 657.

pressure of 10–101 atmospheres. This hydrogenation, therefore, was evidently effected in a gas-solid system.

On the other hand, it was shown by Ipatief(1) that the product from hydrogenation of camphor at 200° under 129 atmospheric pressure in the presence of nickel, melted at 210°. In his experiment camphor was subjected to hydrogenation in melted state which differs from the condition of our investigation and the product seems to be consisting of isoborneol for the most part, with a trace ot borneol. (Melting point: borneol=203°, isoborneol=212°).

Whatever method of reduction may have been taken, the borneol obtained from camphor has been found to contain a certain proportion of isoborneol which varies with the condition of reduction as follows :(2)

Method of reduction	Melting point of the product	Amount of isoborneol
Ethyl alcohol+Na	203°-206°	22.4%
Amyl alcohol+Na	203 -204	19.0%
Phenol+Na	203 -204	21.0%

The result obtained by the catalytic hydrogenation in the presence of nickel (by Ipatief), as compared with that in the presence of copper (by us), is as follows :

Method of reduction	Melting point of the product	Amount of isoborneol
(200°, 129 atm.) Hydrogen+nickel	210°	—
(120°, 92 atm.) Hydrogen+copper	204-205.5°	70.9%

It will be found, thus, that copper is a suitable catalyst for the hydrogenation of camphor by means of hydrogen under pressure and the lower the temperature of reduction, the greater is the yield of borneol.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.

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(1) Ipatief, *J. Russ. Phys. Chem. Soc.*, 38 (1906), 81.

(2) Beckmann, loc. cit.

SPECTROSCOPICAL STUDY OF AMINO-ACID ANHYDRIDES.

I. ON THE CONSTITUTIONS OF SOME SIMPLE AMINO-ACID ANHYDRIDES.

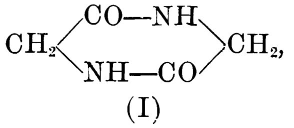
By **Yuji SHIBATA** and **Tei-ichi ASAHINA.**

Received March 12, 1926. Published April 28, 1926.

In the chemistry of protein substances, when it especially concerns to their constitutions, the well known polypeptide theory of Emil Fischer is now going to be replaced by the polymerisation theory of amino-acid anhydrides, as the results of the recent investigations of various biochemists (Trönsegaard, Abderhalden, Bergmann, Karrer, Keita Shibata etc.)

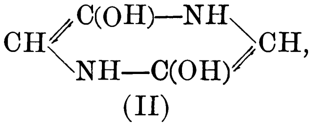
It is, therefore, obvious that the future studies of protein substances and their decomposition products will necessarily be attempted from the point of view of this new theory. In this reason we have undertaken the present investigation with the intention of determining the constitutions of various amino-acid anhydrides, which will be obtained at the end products of depolymerisation of proteins, in applying the spectroscopic method.

As for the constitution of diketopiperazine, which is regarded as the simplest amino-acid anhydride, it may be formulated as follows :



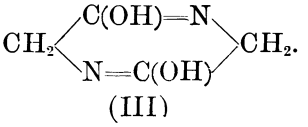
$CH_2\langle\begin{smallmatrix}CO—NH\\NH—CO\end{smallmatrix}\rangle CH_2$,

(I)



$CH\langle\begin{smallmatrix}C(OH)—NH\\NH—C(OH)\end{smallmatrix}\rangle CH$,

(II)



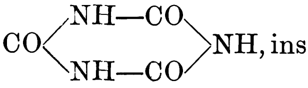
$CH_2\langle\begin{smallmatrix}C(OH)=N\\N=C(OH)\end{smallmatrix}\rangle CH_2$.

(III)

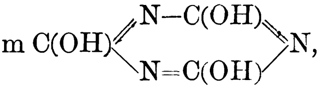
But it has not yet been confirmed which of these three formulae is most probably attributed to the substance, or whether it may take two or even three forms at the same time, or not.

In examining these formulae on the spectrochemical standpoint, we can at once find that each of them contains either of well known chromophore groups : $:C=C:$, $:C=N-$ or $:C=O$; among these, however, it is often noted that the carbonyl group, when two of them occur in the para-position in a saturated haxa-atomic ring, shows no selective absorption in any region of spectrum.

J. N. Hartley⁽¹⁾ observing no absorption band in the spectrogram of cyanuric acid came to the conclusion that this substance must be in the keto-form



$CO\langle\begin{smallmatrix}NH—CO\\NH—CO\end{smallmatrix}\rangle NH$, instead of being in the enol-form



$C(OH)\langle\begin{smallmatrix}N-C(OH)\\N=C(OH)\end{smallmatrix}\rangle N$,

which is analogously constructed as benzene, and therefore should selectively absorb in ultraviolet.

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(1) Hartley *J. Chem. Soc.*, 39 (1881), 153; 41 (1882), 48; *Proc. Chem. Soc.* (1889), 46.

Martinet(1) also states in his book on the chromophoric nature of $C=N-$ group, in describing as follows: "Lorsque le chromophore $C=N$ se trouve dans un cycle, il est, comme dans une chaine ouverte, plus favorable à la coloration qu'une double liason entre atomes de carbone." It is clear that by "coloration" he means any selective absorption.

Now, the spectrogram of some simple diketopiperazines, such as glycine anhydride, alanine anhydride and sarcosine anhydride, which were studied by us, showing no absorption band in any part of spectrum region, it may be concluded from the reasons just mentioned, that these diketopiperazines exist only in keto-form (I) in aqueous solution.

The diketopiperazines used in the present study were mainly prepared by heating the corresponding amino-acids in glycerol according to the method given by Balbiano(2) and also by Maillard.(3)

Experimental.

Glycin Anhydride. Glycine was prepared according to a method given by Kraut(4); the substance, which was purified by five times recrystallisations from water, is remarkably discoloured, when heated, at 226° and begins to melt at 232°, evolving brownish vapour. Glycine (2–6 gr.) was then well mixed with 1–6 times of glycerol, which was thoroughly dehydrated, and the mixture was kept in temperatures of 160–180° for 4–10 hours in an oil bath. On cooling the darkbrownish viscous liquid thus formed was treated with ethyl alcohol and the produced precipitates were filtered. This dark coloured mass was washed with water and from the wash liquid diketopiperazine was obtained and purified by recrystallisations from water.

When a sufficient quantity of glycerol was not used, the yield of diketopiperazine thus produced should remarkably be diminished, giving rather larger quantity of polymerised anhydride. In order to obtain a good yield of diketopiperazine the quantity of glycerol employed must be at least five times of that of glycine.

The anhydride purified by repeated recrystallisations began to be discoloured at 262° and was completely decomposed at 295°. The nitrogen content was determined by Pregl's micro-Dumas method: 4.464 mg. of sample gave 0.956 c.c. of nitrogen at 20° under 765.9 mm. (Found: $N=24.7$. $C_4H_6O_2N_2$ requires $N=24.6\%$).

A 0.001 mol solution was spectroscopically examined using Adam-

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(1) Martinet, "Couleur et Constitution chimique," G. Doin, Paris, (1924), p. 74.

(2) Balbiano and Frasciati, *Ber.*, 33 (1900), 2323; 34 (1901), 1501.

(3) Maillard, *Compt rend.*, 153 (1911), 1078.

(4) Kraut, *Ann.*, 266 (1891), 292.

Hilger's quartz spectrograph. In this spectrogram, however, we could find no selective absorption all through the spectrum region, that is to say, the solutions of this substance with varying thicknesses from 100 to 1 mm. were quite transparent to extreme ultraviolet. A feebly alkaline solution of diketopiperazine of 0.001 mol concentration was also photographed in order to examin whether the substance change its constitution in alkaline medium or not. But it was also proved from its spectrogram that this was by no means the case.

The Anhydride of Alanine (C, C'-dimethyldiketopiperazine). 3.2 gr. of alanine was mixed with 6 c.c. of glycerol and the mixture was heated in an oil-bath at 170–180° for about 5 hours. Soon all crystals of alanine were dissolved, ammonia and carbon dioxide were evolved and the liquid turned slightly reddish brown. From this viscous liquid, crystals were separated out on cooling. After repeated recrystallisation from water, colourless fine crystals with silvery lustre were obtained. In this case polymerised anhydride was not produced. The crystals began to be discoloured at about 260° and melted, under slight decomposition, at 279°. Analysis of nitrogen : 2.575 mg. of sample gave 0.440 c.c. nitrogen at 19° under 766.2 mm. (Found : N= 19.8. $C_6H_{10}N_2O_2$ requires N=19.7%). A 0.001 mol solution of this anhydride (0.0142 gr. in 100 c.c. water) was examined spectroscopically, but no absorption bands were observed in its spectrogram.

Sarcosine Anhydride (N, N'-dimethyldiketopiperazine). 2 gr. of sarcosine was well mixed with 20 gr. glycerol and heated at 170–180°. Soon sarcosine was completely dissolved, methylamine vapour and carbon dioxide were evolved, and the liquid became brown in colour. After 9 hours heating the liquid was cooled, shaken with acetic ester two or three times, and, by evaporating off the ester, some crystals were obtained (0.5 gr.) After recrystallisation from absolute alcohol, it melted at 145.5–146.5°. Dry distillation of 4 gr. of sarcosine also gave 1 gr. of crystals in the distillate.(1) Its melting point was 144.5–145.5°. The melting point did not lower on mixing these two specimens, thus identity of these two products was confirmed. The analysis of nitrogen : 4.622 mg. of substance gave 0.794 c.c. of nitrogen at 18.5° under 757.2 mm. (Found : N=19.7. $C_6H_{10}N_2O_2$ requires N=19.7%). 0.1421 gr. of the anhydride was dissolved in 100 c.c. of water (0.01 mol solution) and was examined spectroscopically. In this case too, no selective absorption could be observed in its spectrogram.

Summary.

Some simple amino-acid anhydrides were prepared after Maillard's method and were examined spectroscopically. So far as the present investi-

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(1) F. Mylius, *Ber.*, **17** (1884), 287.

gation is concerned, it was proved that the solutions of these amino-acid anhydrides show no selective absorption. From this fact we came to the conclusion that these substances are considered to be only in keto-form in aqueous solution.

The experiment is going on with other amino-acids. We express herewith our best thanks to Prof. Keita Shibata's kind advices. The cost of this investigation was defrayed from the grant of the Imperial Academy, for which we wish to record our gratefulness.

December 1925.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

ON THE TERPENE AND THE SESQUITERPENE OF MITSUBAZERI. PRELIMINARY REPORT.⁽¹⁾

By Nenokichi HIRAO.

Received March 16, 1926. Published April 28, 1926.

Cryptotaenia japonica Hassk (*Umbellifer.*), domestically known as mitsubazeri, grows naturally in forests and in shady places, and is also cultivated in the kitchen-garden as one of the greens. So far as I am aware, the essential oil of this plant does not appear to have been described. The present author began its investigation in the year 1924, and is now obliged to discontinue the work for a short time. Accordingly, the results already obtained, though somewhat imperfect, are published as a preliminary report.

To isolate the essential oil, it was distilled in steam, for when the plant is digested with water, the fragrance becomes stronger. The author thus obtained 128 gr. of an oil from 1125 kilo. of fresh mitsubazeri. On fractionating repeatedly under reduced pressure, the oil separated into two fractions, one boiling at 67–68°/15 mm., and the other, at 142–143°/15 mm. The author proposes to designate the former cryptotaenene, and the latter, mitsubaene.

Whilst cryptotaenene is a terpene having the composition $C_{10}H_{16}$, mitsubaene is a sesquiterpene of the composition $C_{15}H_{24}$. These two hydrocarbons have the odour characteristic of mitsubazeri. The odour of mitsubaene is much more pronounced than that of cryptotaenene.

With the object of obtaining their crystalline derivatives, attempts were

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(1) This communication is the thesis for graduation at the Tohoku Imperial University.

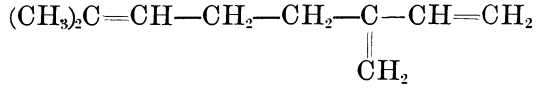
made to prepare bromide, hydrochloride, nitrosite or nitrosate, but without success. The molecular refraction points to the presence of three double bonds in cryptotaenene, together with the formation of triozonide by the action of ozone on the substance. As, however, four atoms of bromine add to one molecule of cryptotaenene, it would appear that it contains a conjugated double bond.

The cryptotaenene triozonide was first decomposed with water, as it was expected that this would throw considerable light on the constitution of cryptotaenene.

The author isolated, as its decomposition products, carbon dioxide, formic acid, acetone, acetone peroxide, succinic acid, and a carbonyl compound which has not yet been determined. Taking into account the fact that α-ketonic acid, RCOCOOH, is oxidised by hydrogen peroxide to a monocarboxylic acid, RCOOH,⁽¹⁾ the constitutional formula of cryptotaenene must be one of the following.

$$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH{=}CH_2 \qquad \text{(I)}$$

$$(CH_3)_2C{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \qquad \text{(II)}$$



$$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}\underset{\underset{CH_2}{\|}}{C}{-}CH{=}CH_2 \qquad \text{(III)}$$

Formula (III) is identical with that of myrcene.⁽²⁾ Since cryptotaenene is quite different from myrcene in physical properties, the constitutional formula of cryptotaenene must be either (I) or (II). If this conclusion be correct, oxalic acid should be one of the decomposition products of cryptotaenene triozonide. However, its absence is accounted for by the fact that oxalic acid is decomposed by hydrogen peroxide.⁽³⁾

For the further determination of the constitutional formula, cryptotaenene was first partially reduced with hydrogen, using platinum black as the catalyser and then the product was converted into ozonide and decomposed with water. However, the quantity of decomposition products was too small to make it possible to decide between (I) and (II), owing to the small quantity of the starting substance at my disposal.

From the determination of molecular refraction and the results of the addition of bromine, mitsubaene seems to be a sesquiterpene with two double bonds. In the investigation of sesquiterpenes, Ruzicka and his collaborators⁽⁴⁾ obtained either cadaline or eudaline by heating a sesquiterpene with sulphur. The author applied this method to mitsubaene and obtained a

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(1) *Rec. Trav. Chim.*, 23 (1904), 169.

(2) T. Brooks, "The Nonbenzenoid Hydrocarbons," p. 182.

(3) Beilstein, "Handbuch der org. Chem.," 4 Auflage, II, p. 508.

(4) *Helv. Chim. Acta.*, 4 (1921), 505; 5 (1922), 345.

liquid, which produced a picrate melting at 90°, identical with the melting point of eudaline picrate. Mitsubaene is thus a sesquiterpene of the eudesmol type. Moreover, the action of ozone on mitsubaene was investigated in order to determine its constitutional formula, and carbon dioxide and formic acid were isolated as the decomposition products of its ozonide.

The further investigation of cryptotaenene and of mitsubaene will be proceeded with as soon as a sufficient supply of the raw material is available.

Experimental.

(1) Three kilo. of fresh mitsubazeri, still edible and about 21 to 24 cm. long, was cut into 3 cm. long and distilled in steam, when the essential oil easily passed over and after 1.5–2 hours the residue had not the characteristic odour of mitsubazeri. The distillate was extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate and evaporated. The quantity of residual oil amounted to 0.21 gr.

(2) Six kilo. of fresh mitsubazeri, not edible and 30 to 75 cm. long were dried for eight days in a shady place and treated in the manner described in (1), when 0.47 gr. of the essential oil was obtained.

From these experiments, it seems that the content of the oil increases with the growth of the plant.

The author obtained 128 gr. of the crude oil from 1125 kilo. of the latter sample by using the second method. On the fractional distillation of the oil under reduced pressure, the following two main fractions were collected :

(a) b.p. 65– 75° under 12–15 mm. ca. 50%
(b) b.p. 135–145° under 12–15 mm. ca. 35%

Cryptotaenene.

On repeating the fractional distillation of fraction (a) under reduced pressure, cryptotaenene was obtained as a colourless mobile oil, b. p. 67–68° under 15 mm., $d_4^{25}=0.8128$, $n_D^{25}=1.47476$, molecular refraction 47.14. $C_{10}H_{16}$, $|^{=}_3$ requires 46.98 (Found : $C=87.75$; $H=11.78$; Mol. wt., cryoscopic in benzene. 132, 135. $C_{10}H_{16}$ requires $C=88.24$; $H=11.76\%$; Mol. wt., 136). Yield : 35 gr.

Determination of the Number of Double Bonds. Addition of Bromine.—An excess of chloroform solution of bromine of known strength was added to a solution of cryptotaenene in the same solvent and, after ten minutes, potassium iodide solution and dilute sulphuric acid were added, and the liberated iodine was titrated with a N/10-sodium thiosulphate solution :

0.1682 absorbed 0.3420 of bromine.

$C_{10}H_{16}$, with two ethylenic linkings, requires 0.3750 of bromine.

Ozonide.—Through a solution of 1 gr. of cryptotaenene in 10 c.c. of chloroform, cooled with a mixture of ice and salt, a current of oxygen containing ca. 5% ozone was passed, at the velocity of 13–14 litres per hour for four hours until no more bromine was absorbed, a current of dry carbon dioxide being passed through it during the operation in order to avoid an explosion. The chloroform was distilled under reduced pressure without the application of heat, when about two grams of ozonide remained behind as a pale yellow oil with a pungent odour. The ozonide was repeatedly purified by dissolving it in a small quantity of ethyl acetate and precipitating with petroleum ether (b.p. 30–60°). The ozonide thus purified was nearly colourless, and was dried over concentrated sulphuric acid in a vacuum desiccator for two days, and then analysed with the following results (Found : C=43.36, 43.66 ; H=5.46, 6.00, $C_{10}H_{16}$, $3O_3$ requires C=42.86 ; H=5.71%).

The Decomposition of the Ozonide. The ozonide obtained from ten grams of cryptotaenene, together with four to five times its weight of water, was put into a flask provided with a reflux condenser, the latter being successively connected with two flasks, the one (A) containing 40 c.c. of cold water and the other (B), 300 c.c. of cold solution of ca. N/5 baryta solution, in order to retain any volatile and gaseous products that might be formed during the decomposition. The flask was carefully warmed over a water-bath, a slow current of hydrogen being passed through the whole apparatus.

On the addition of a solution of p-nitrophenylhydrazine in dilute hydrochloric acid to the contents of the flask (A), a p-nitrophenylhydrazone was obtained, which, after recrystallisation from benzene, melted at 148°, and produced no depression of the melting point on admixture with acetone p-nitrophenylhydrazone, thus leaving no doubt as to its identity with acetone p-nitrophenylhydrazone.

In the flask (B), barium carbonate was precipitated. After filtering off the precipitate, the excess of the baryta in the filtrate was titrated with N/2-sulphuric acid. The quantity of carbon dioxide amounted to 0.5 or 0.55 gr. in two separate experiments.

There was a deposit of a small quantity of a crystalline substance on the lower part of the reflux condenser. After drying this deposit in a desiccator, it melted at 132° and was identified as acetone peroxide by the method of mixed melting point.

The aqueous solution of the decomposition products was distilled in steam, and the distillate (C) and the residue (D) were treated as follows :

The distillate (C) was contaminated with an oily matter with a pleasant odour, which, owing to the lack of available substance, could not be determined. In order to isolate any neutral decomposition products, the distillate, after removing the oil and neutralising it with baryta solution, was again distilled in steam and subjected to fractional distillation, when the following fractions were collected: (1), b.p. below 100°; and (2), b.p. above 100°.

Fraction (1) (b.p. below 100°).—This fraction, on being mixed with a solution of p-nitrophenylhydrazine in hydrochloric acid, precipitated about one gram of a p-nitrophenylhydrazone. The p-nitrophenylhydrazone, after being recrystallised from benzene, melted at 148.5° and was identified as acetone p-nitrophenylhydrazone by the method of mixed melting point and by analysis (Found: $N=21.93$. $C_9H_{11}O_2N_3$ requires $N=21.76\%$).

Fraction (2) (b.p. above 100°).—This fraction was mixed with a solution of p-nitrophenylhydrazine in hydrochloric acid, and allowed to stand for several days, when reddish brown crystals were deposited which are soluble with difficulty in ordinary organic solvents and discoloured at about 250° without melting. The crystals have not been further investigated owing to the small amount of material available.

The barium salt remaining in the distillation flask was evaporated to dryness on the water-bath, and the residue acidified with sulphuric acid (1 : 3). After filtering off barium sulphate, the filtrate was distilled under ordinary pressure. The fraction distilled at below 105° which showed marked reactions of formic acid, was neutralised with solid lead carbonate, and filtered. After evaporating the filtrate to a small bulk, colourless needles (5 gr.) were obtained, which were recrystallised from hot water and analysed with the following results (Found: $Pb.=69.37$. $(HCOO)_2Pb$ requires $Pb=69.72\%$).

Formic acid was thus established as one of the decomposition products.

Products Non-volatile in a Current of Steam. The residue (D) was first extracted with ether and the ethereal solution (E) and the aqueous residue (F) were treated in the following way:

The ethereal solution (E) was shaken with a solution of sodium bicarbonate, in order to isolate any acidic substances. No neutral or acidic substance was obtained in the pure state from either the etherealor the bicarbonate solution.

The aqueous residue (F) was concentrated to a small bulk and allowed to stand, when crystals (0.8 gr.) and viscid oil (1 gr.) were obtained. The crystals were recrystallised from water with the addition of animal charcoal, when they separated as colourless crystals melting at 183° and were proved to be succinic acid by the method of mixed melting point.

Nothing definite could be isolated from the viscid oil.

Mitsubaene.

On fractionating fraction (b) repeatedly under reduced pressure, mitsubaene was obtained as a faint yellow oil, b.p. 142–143° under 15 mm., $d_4^{25}=0.9175$, $[\alpha]_D^{21.9}=+8.31$, $n_D^{25}=1.50381$, molecular refraction 65.90. $C_{15}H_{24}$, $|^{=}_{2}$ requires 66.13 (Found: C=88.07; H=11.83; Mol. wt., cryoscopic in benzene, 198, 207. $C_{15}H_{24}$ requires C=88.24; H=11.76%; Mol. wt., 204). Yield: 27 gr.

Thus, mitsubaene has two ethylenic linkings, which result is in agreement with that obtained from the addition of bromine.

Addition of Bromine.—The amount of bromine to be added to mitsubaene was estimated in a manner exactly similar to that employed in the case of cryptotaenene:

0.1062 absorbed 0.1946 of bromine, whereas $C_{15}H_{24}$, with two ethylenic linkings, should require 0.1663 of bromine.

The Action of Sulphur on Mitsubaene. A mixture of 5 gr. of mitsubaene and 2.1 gr. of sulphur was heated to 180–220° in the oil-bath under a reflux condenser. After six hours' heating, the product was distilled under diminished pressure. The distillate was redistilled over metallic sodium under reduced pressure, when 0.5 gr. of oil boiling at 143–147° under 15 mm. passed over, from which a picrate was isolated by adding an alcoholic solution of picric acid. The crude picrate was twice recrystallised from alcohol, when it separated in orange crystals melting at 90°, identical with that of the eudaline picrate.

Ozonide of Mitsubaene. Through mitsubaene dissolved in ten times its volume of dry chloroform, a current of oxygen containing 5% of ozone was passed, until a solution of bromine in chloroform was no longer decolourised, care being taken to avoid the rise of temperature during the ozonisation by cooling it with ice and salt. The chloroform was evaporated under reduced pressure without the application of heat, when a yellow, viscid oil remained behind, which was purified by dissolving it in chloroform and precipitating with petroleum ether. The ozonide thus purified was dried over concentrated sulphuric acid in a vaccum desiccator for two days. As, however, the ozonide decomposed, no decisive results as to the number of double bonds were obtained by analysis.

On decomposing the ozonide by warming it with water, the author isolated carbon dioxide and formic acid.

In conclusion, the author wishes to express his gratitude to Dr. Hiroshi Nomura for his kind guidance during the progress of this investigation.

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THE ACTION OF PROTECTING COLLOIDS ON MERCURIC IODIDE.

By Jitsusaburo SAMESHIMA and Takeo SUZUKI.

Received March 3, 1926. Published May 28, 1926.

J. N. Friend(1) described that the mercuric iodide deposited from the mercuric chloride and the potassium iodide solutions in the presence of gelatine is the yellow modification. We have done some experiments on this subject which is described in the following.

When 1 c.c. of 0.1 normal mercuric chloride solution and 1 c.c. of 0.1 normal potassium iodide solution are added to 100 c.c. of 0.0025% gelatine solution, the deposition of mercuric iodide is considerably retarded, but the deposited iodide is ordinary red modification.

When 1.5 c.c. of 0.1 normal mercuric chloride and potassium iodide solutions are added to 100 c.c. of 0.005% gelatine solution, there appears pink coloured turbidity, which, after a while, separates itself into a red precipitate and a white turbid liquid.

When 1.5 c.c. of 0.1 normal mercuric chloride and potassium iodide solutions are added to 0.01% (or more concentrated) gelatine solution, an yellow precipitate appears, which then changes to white. This white substance again changes to the red precipitate after several days.

The yellow precipitate is a modification of mercury iodide which is stable at the temperature higher than 127°. If the pure mercuric chloride and pure potassium iodide solutions are mixed together, the yellow precipitate will appear at first, but it instantaneously changes to the stable red form. If, however, there is a protecting colloid such as gelatine in the solution, then the yellow particles will quickly be enveloped by the colloid, and are prevented to change to the stable modification. The gelatine envelope will prevent the contact of the yellow particles to each other, so the crystal nuclei of red modification can not grow itself, as can be seen in the case of large crystals or a fused mass of mercuric iodide.(2) Moreover, the solubility of the unstable yellow form in water is, of course, greater than that of the stable red form in water, but the rate of solution will considerably be retarded when the particles are wrapped by the gelatine films. So the rate of growing of the stable crystal by the expense of the unstable one will also be retarded.

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(1) J.N. Friend, *Nature*, 109 (1922), 341.

(2) Damiens, *Compt. rend.*, 177 (1923); 178 (1924), 326.

The white precipitate is probably the addition compound of yellow mercuric iodide and gelatine though this is not a stable substance but decomposes into red mercuric iodide and gelatine after a few days.

When 4 c.c. of 0.1 normal mercuric chloride and 4 c.c. of 0.1 normal potassium iodide solutions are added to 100 c.c. of 0.025% gelatine solution, the white liquid has the appearance of the milk. The white substance was separated from the liquid by using a centrifugal machine, and dried and weighed. The dried mass was heated to 400° to decompose the gelatine, and the sublimed mercuric iodide was dissolved into the potassium iodide solution. Then the mercury was estimated by passing hydrogen sulphide in this solution. By this analysis we have seen that the white precipitate was composed of 93% of mercuric iodide and 7% of gelatine, and that 1/4 of the whole gelatine in the solution combined with mercuric iodide.

In the next place, we have examined the protecting action of other colloidal substances than gelatine. The milk, the albumen, the legumine, the extracts of meats, the human saliva, the extracts of vegetables, the solution of wheat flour, etc. have the protecting power on the yellow mercuric iodide. Among these the egg albumen and the extract of the fish have the strongest protecting power, and the mercuric iodide produces not only as the yellow modification but also as an yellow transparent colloidal solution. The agar, the sodium silicate, the starch, the soap, the dextrin, the glycerin, the cane sugar, the urea etc. show no protecting action on yellow mercuric iodide, and precipitate the red form instantaneously.

Generally, we can say that the albuminous substances have the protecting action in this case.

In the following table, the "gold number" of various colloidal substances are compared with their protecting power on the yellow mercuric iodide. The gold number has been determined by the method given by Zsigmondy.(1) The protecting power on mercuric iodide was measured by the quantity of protecting colloid which is necessary to keep the substance in yellow form for 20 minutes, when 5 c.c. of 0.1 normal mercuric chloride and 5 c.c. of 0.1 normal potassium iodide solutions are added to 100 c.c. of water which contains the protecting colloid.

Protecting colloid	Gold number	Protecting power on yellow mercuric iodide
Gelatine	0.009	0.002 gr.
Egg albumen	0.1-0.4	0.01 gr.
Meat extract	1.	0.005 c.c.
Legumine solution	2.	0.1 c.c.
Gum arabic	0.05-0.08	10. gr.
Carrot extract	800.-1000.	50. c.c.

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(1) Zsigmondy, "Kolloidchemie," (1922), p. 174.

Protecting colloid	Gold number	Protecting power on yellow mercuric iodide
Agar	0.08–0.1	No action
Sodium oleate	0.8–1.1	No action
Starch	2.	No action
Dextrin	9.–12.	No action
Silicic acid	∞	No action

Thus the protecting action on the colloidal gold and on the yellow mercuric iodide are not quite parallel. The colloids which contain much nitrogen compounds have great protecting power on the yellow mercuric iodide.

A part of the present experiment was done in the chemical laboratory of the Tohoku Imperial University, Sendai.

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ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. II.(1)

By San-ichiro MIZUSHIMA.

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As the result of the preliminary experiment it was found that several alcohols, monovalent as well as polyvalent, show anomalous dispersions of the electric wave of 6.1 meters accompanied by anomalous absorptions.(2) Similar experiments were carried out with the wave of 9.5 meters. In this case the values of the dielectric constants were calculated introducing proper corrections to direct observations. Also the values of anomalous absorptions were expressed in terms of electric conductivities which are equivalent to them.

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(1) Read before the Chemical Society of Japan, April 5, 1926.

(2) This journal, 1 (1926), 47.

The oscillating circuit as well as the resonating are quite similar to that used in the case of the wave of 6.1 meters. Fig. 1 shows the resonating circuit.

Measurement of Absorption. If the substance under investigation is non-absorbent, the value I/I_0 (I and I_0 being the deflections of the galvanometer G at the resonance when X is filled with the substance and the air respectively) is always unity, provided that the inductance of the leading wires from C to X is very small. If the substance is an absorbent, I/I_0 is necessarily less than unity, and depends upon the electric capacity of X. To find the expression of the anomalous absorption depending only upon the characteristics of each substance this is replaced by an equivalent normal absorption (*i.e.* an absorption which is caused only by the electric conductivity), and the specific conductivity of the latter is taken as the measure of the former.

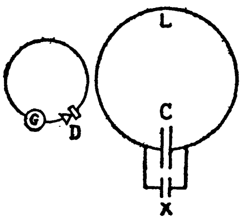

Fig. 1.

A series of experiments showed first of all that water and acetone do not absorb the wave of 9.5 meters and secondly that when the salts such as NaCl, KI, etc. are dissolved in them, the value of I/I_0 depends almost only upon the electric conductivity of the solution. For example the acetone solution of KI and the aqueous solution of NaCl, having the same conductivity, show the same value of I/I_0. These solutions can be used, therefore, as the standards to compare the two kinds of absorptions. The values I/I_0 with respect to corresponding electric conductivities were measured with the acetone solution of KI and the result is shown in Table 1.

TABLE 1.

Approximate Dilution of KI mol per litre	Specific Conductivity $cm^{-1}\ ohm^{-1}$	I/I_0 Vessel I	I/I_0 Vessel II	I/I_0 Vessel III	I/I_0 Vessel IV
240	48×10^{-5}	0.04	0.03	—	—
480	26×10^{-5}	0.08	0.06	0.05	0.04
960	14×10^{-5}	0.16	0.12	0.10	0.09
1920	7×10^{-5}	0.28	0.22	0.19	0.18
3840	3.5×10^{-5}	0.48	0.38	0.35	0.34
7680	1.8×10^{-5}	0.66	0.57	0.55	0.55

Measurement of Dielectric Constant. The value of the dielectric constant ε of a non-absorbent can be obtained from the displacement ΔC of the glass plate of the variable capacity C (Fig. 1). But if the substance is an absorbent, ΔC corresponds to a capacity shunted by a conductivity. Therefore to calculate the value of ε of such a substance from ΔC, the correction which corresponds to this conductivity should be known. In the present experiment the following method was adopted.

Recently Walden⁽¹⁾ studied the change of the dielectric constant between a pure solvent and a solution obtained by dissolving a salt in it, and found that the change is less than a few percent for an organic solvent when the dilution of the salt is as shown in Table 1. The result was confirmed by the experiment on the acetone solution of KI which is described in the following.

A glass vessel which consists of two parts A and B is constructed (Fig. 2). Two platinum wires are sealed in both parts so that the main part of electric capacity lies in A and only a small part in B. The electric capacity is determined in the following three cases; (a) when both A and B are filled with pure acetone, (b) when both A and B are filled with the acetone solution of KI (of a dilution as shown in Table 1.) and (c) when A is filled with pure acetone and B with a solution of such a concentration that the total conductivity is equal to that in the case of (b). The apparent change of capacity caused by the conductivity in the latter two cases should be equal to each other. Therefore the change of the dielectric constant between the solvent and the solution can at once be known if there is any difference of ΔC in these two cases. The result of the experiment shows that no difference can be found within the experimental error which amounts to a few percent, though the value in these two cases is quite different from that in (a). The change of the dielectric constant of acetone can safely be neglected and the correction for the conductivity can be obtained from the difference between ΔC in (a) and that in (b). Table 2 contains the experimental values of ΔC and $\Delta^2 C$ (the difference between ΔC of the solution and that of pure acetone) obtained at the room temperature when the solutions of various conductivities are contained in the vessels I, II, III and IV of X.

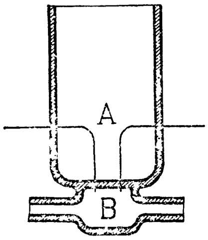

Fig. 2.

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(1) Walden, *Z. physik. Chem.*, **115** (1925), 177; **116** (1925), 261.

TABLE 2.

Conductivity cm^{-1} ohm^{-1}	Vessel I		Vessel II		Vessel III		Vessel IV	
	ΔC	$\Delta^2 C$	ΔC	$\Delta^2 C$	ΔC	$\Delta^2 C$	ΔC	$\Delta^2 C$
48×10^{-5}	3.5	0.9	4.6	1.4	—	—	—	—
26×10^{-5}	3.05	0.45	3.7	0.5	4.55	0.7	5.5	0.9
14×10^{-5}	2.75	0.15	3.4	0.2	4.1	0.25	4.9	0.3
7×10^{-5}	2.65	0.05	3.25	0.05	3.9	0.05	4.7	0.1
3.5×10^{-5}	2.6	0	3.2	0	3.85	0	4.6	0
pure acetone	2.6	—	3.2	—	3.85	—	4.6	—

The aqueous solutions of NaCl etc. give the same result as above, *i.e.* the acetone solution of KI and the aqueous solution of NaCl give the same value of $\Delta^2 C$ when the two have the same conductivity and are contained in the same vessel. Hence $\Delta^2 C$ depends merely upon the conductivity of the medium. Thus $\Delta C'$, the corrected value of the displacement ΔC of the glass plate, from which the dielectric constant is to be calculated, can be simply found from the following equation,

$$\Delta C' = \Delta C - \Delta^2 C$$

$\Delta^2 C$ is to be found graphically for each vessel, combining tables 1 and 2, the value I/I_0 being known from a direct observation.

Experimental Results. The wave length was determined with various combinations of inductance and capacity and the result is shown in Table 3.

TABLE 3.

Inductance cm. (E.M.U.)	Capacity cm. (E.S.U.)	Wave length m.
104	22.0	9.50
115	20.0	9.53
127	17.8	9.45

The wave length is, therefore, 9.5 meters.

The experimental data on the non-absorbents, acetone and ether, and the absorbent glycerine are given in the following tables.

I/I_0 : Ratio of the deflections of galvanometer at resonance,
ΔC : Displacement of glass plate,
$\Delta C'$: Corrected value of ΔC,
ε : Dielectric constant,
K : Electric conductivity which is equivalent to anomalous absorption (cm^{-1} ohm^{-1}).

TABLE 4.

Ethyl ether

Vessel	Temp.	I/I_0	ΔC	ε	ε* (Isnardi)
VII	5	1.0	6.25	4.7	4.6
VI	5	1.0	4.3	4.8	4.6
VII	−24	1.0	7.8	5.6	5.5
VI	−24	1.0	5.2	5.6	5.5
VII	−60	1.0	10.0	6.8	6.6
VI	−60	1.0	6.4	6.6	6.6

TABLE 5.

Acetone

Vessel	Temp.	I/I_0	ΔC	ε	ε† (Graffunder)
I	20	1.0	2.55	21	22.4
II	20	1.0	3.2	22	22.4
I	8	1.0	2.8	23	23.9
II	8	1.0	3.55	24	23.9
III	7	1.0	4.05	24	23.9
IV	7	1.0	4.8	24	23.9
III	− 5	1.0	4.3	25	24.5
IV	− 5	1.0	4.8	24	24.5
I	−13	1.0	3.15	25	25.3
II	−13	1.0	3.9	26	25.3
IV	−15	1.0	5.35	26	25.4
III	−15	1.0	4.65	26	25.4
IV	−47	1.0	6.3	29	
III	−47	1.0	5.45	29	
II	−48	1.0	4.75	30	
I	−48	1.0	3.95	30	
III	−51	1.0	5.25	28	
IV	−51	1.0	6.1	28	
III	−66	1.0	5.8	31	
IV	−67	1.0	6.65	30	

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* These values of ε are obtained by graphical interpolation.
Isnardi, *Phys. Z.*, 22 (1921) 230.

† These values of ε are obtained by graphical interpolation.
Graffunder, *Ann. Physik.* 70 (1923), 225.

TABLE 6.

Glycerine

Vessel	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K\times10^5$	ε* (Graffunder)
II	65	5.25	.72	5.25	36	<1	35.2
I	59	4.45	.74	4.45	38	1	36.2
II	50	5.65	.50	5.65	39	2	37.7
I	40	4.9	.48	4.9	41	3	39.4
II	31	6.15	.23	6.15	41	7	40.9
I	25	5.1	.21	5.1	41	10	41.9
II	24	6.4	.14	6.25	42	12	42.0
I	23	5.25	.18	5.2	43	12	42.3
I	22	5.2	.15	5.1	42	15	42.5
I	14	4.95	.09	4.6	37	24	44.0
II	13	5.95	.07	5.5	36	23	44.1
II	12	5.65	.07	5.2	34	23	44.3
I	12	4.55	.09	4.2	34	24	44.3
II	11	5.85	.06	5.3	35	26	44.5
IV	4	6.8	.04	5.9	29	26	46.1
I	3	3.75	.08	3.35	27	26	
I	2	2.75	.08	2.35	19	26	
II	0	3.6	.06	3.05	20	26	
I	−4	1.95	.09	1.6	14	24	
I	−9	1.75	.16	1.65	14	14	
II	−11	1.95	.15	1.8	12	11	
IV	−12	2.4	.12	2.2	11	11	
II	−18	1.05	.26	1.05	8	5	
IV	−21	1.4	.29	1.4	8	4	
IV	−24	1.05	.40	1.05	6	3	
II	−30	0.8	.53	0.8	6	2	
II	−33	0.65	.58	0.65	5	2	
IV	−40	0.8	.72	0.8	5	<1	
IV	−41	0.8	.70	0.8	5	1	
II	−51	0.5	.84	0.5	4	<1	
II	−52	0.35	.86	0.35	3	〃	
IV	−58	0.65	.95	0.65	4	〃	
IV	−61	0.5	.98	0.5	3	〃	

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* Graffunder, loc. cit.

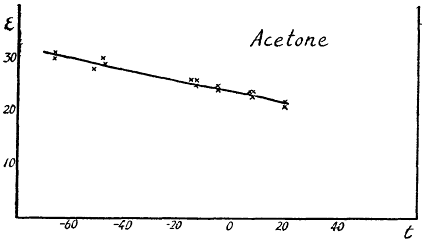

Fig. 3.

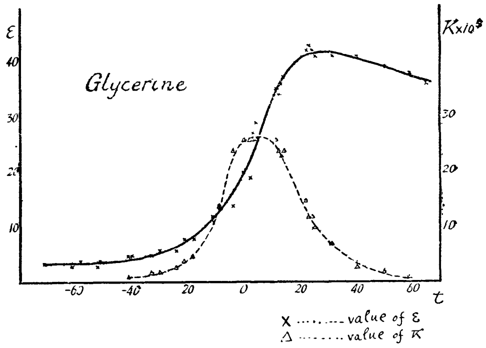

Fig. 4.

Ethyl ether and acetone. (Table 4 and 5, Fig 3). These two substances show no difference between I and I_0 within the limit of the experimental error. The value of ε coincides with that obtained by Isnardi(1) and Graffunder(2) at long wave lengths.

Glycerine. (Table 6, Fig. 4). The anomalous behaviour is quite similar to that at the wave length of 6.1 meters. At low temperatures there is almost no absorption and ε takes a value nearly equal to the square of the refractive indices for the visible light. As the temperature is gradually raised, the absorption of wave takes place, and the value of K increases with ε. K reaches the maximum value at the point where the temperature coefficient of ε is nearly maximum. Then K decreases, but ε still increases till it attains a maximum value. Thence the change of ε is quite normal (i.e. ε decreases as the temperature is raised) and, although there is some absorption in this region, the values of ε obtained are found to coincide with those measured at longer wave lengths.

Further explanation of results will be given in the next paper which will contain the experimental data on monovalent alcohols. The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

October, 1925

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(1) Isnardi, loc. cit.

(2) Graffunder, loc. cit.

ETUDES DE DÉRIVÉS DU FURFURAL.

I. CONDENSATION DU FURFURAL AVEC LES CÉTONES ALIPHATIQUES.

Par Itizo KASIWAGI.

Reçu le 27 février 1926. Publié le 28 mai 1926.

L'analogie du furfural avec le benzylal est très remarquable, et des condensations semblables ont lieu, donnant naissance à des produits semblables. On peut classer en plusieurs types les condensations attribuées aux groupements carbonyles que donnent les deux aldéhydes sous l'influence de divers catalyseurs, et nous en mentionnerons ici trois seulement :

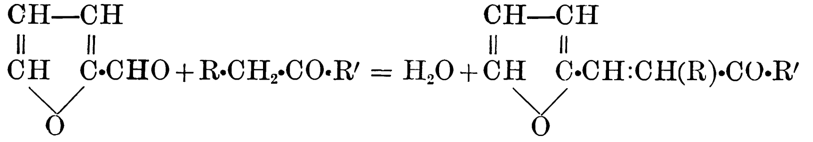
1° Condensation des groupements carbonyles entre eux⁽¹⁾,

2° Condensation des groupements carbonyles et des aldéhydes⁽²⁾,

3° Condensation des groupements carbonyles et des cétones⁽³⁾.

Sous l'action des alcalis le furfural se combine avec les cétones toujours de façon que l'oxygène du premier s'élimine à l'état d'eau en se combinant avec les deux atomes d'hydrogène du radical CH, CH_2 ou CH_3 qui est lié au voisinage du groupement fonctionnel CO des deuxièmes. La condensation avec les cétones peut avoir lieu entre les aldéhydes citées ci-dessus et les cétones aliphatiques⁽³⁾, aromatiques⁽⁴⁾, ou cyclaniques⁽⁵⁾. Bien que cette condensation puisse être utile pour constater l'existence du groupe CH_2 voisin du carbonyle dans les molécules⁽⁶⁾, la réaction entre le furfural et les cétones — surtout cétones aliphatiques — a été peu étudiée.

Conséquemment nous avons étudié la condensation du furfural avec divers termes de la série des cétones grasses, dont la réaction en présence des alcalis caustiques peut être exprimée par l'équation ci-dessous :



$$\begin{array}{llll} \mathrm{CH{-}CH} & & \mathrm{CH{-}CH} & \\ \Vert\quad\ \Vert & & \Vert\quad\ \Vert & \\ \mathrm{CH\quad C{\cdot}CHO} & + \mathrm{R{\cdot}CH_2{\cdot}CO{\cdot}R'} = \mathrm{H_2O} + & \mathrm{CH\quad C{\cdot}CH{:}CH(R){\cdot}CO{\cdot}R'} & \\ \quad\diagdown\diagup & & \quad\diagdown\diagup & \\ \quad\ \mathrm{O} & & \quad\ \mathrm{O} & \end{array}$$

Cette réaction, c'est-à-dire la formation des cétones furyliques non saturées est

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(1) Par exemple, la formation de la furoine, la réaction de Cannizzaro, c'est-à-dire la formation de l'alcool et de l'acide sous l'alcali caustique, ou sous l'amidure de sodium (Kasiwagi, Ce journal, 1 (1926), 66) etc.

(2) D. Ivanoff, *Bull. soc. chim.*, (4), 35 (1924), 1658.

(3) Schmidt, *Ber.*, 14 (1881), 1459.
Claisen, *Ber.*, 14 (1881), 2469.

(4) Kostanecki et Podrajansky, *Ber.*, 29 (1896), 2249.

(5) Mlle. N. Wolf, *Ann. chim.*, (9), 20 (1923), 83.

(6) H. Meyer, " Analyse u. Konstitutionsermittlung," 3ème édition (1916), 706.

probablement précédée de la formation des cétols correspondants, qui, par perte d'eau, donnent des cétones non saturées. Les cétols ne sont que les produits d'addition de l'aldéhyde avec les cétones, dont les réactions dépendent, sous l'influence des alcalis, de la tendance migratrice de l'atome d'hydrogène lié à l'atome de carbone au voisinage du groupe CO. Cet atome d'hydrogène se fixe ainsi sur l'atome d'oxygène de l'aldéhyde.

Par conséquent, il est évident qu'une cétone ne possedant qu'à un faible degré cette tendance migratrice ne réagit que difficilement sur l'aldéhyde ou à la faveus d'un agent énergique. Le camphre ne se combine pas avec l'aldéhyde sous l'action des alcalis caustiques, ou de l'alcoolate de sodium,(1) mais il condense avec elle seulement au moyen de l'amidure de sodium.(2)

Partie expérimentale.

La condensation du furfural avec l'acétone sous l'action des alcalis caustiques, fut déjà étudiée par Schmidt(3) et par Claisen(4) et elle est exprimée par la formule :

$$C_4H_3O{\cdot}CHO + CH_3{\cdot}CO{\cdot}CH_3 = H_2O + C_4H_3O{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3 \qquad (I)$$

Cependant, au fur et à mésure de la quantité croissante de furfural, la furyl-1-butén-1-one-3 formée (I) réagit encore avec l'aldéhyde pour donner

$$\begin{aligned}&C_4H_3O{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3 + C_4H_3O{\cdot}CHO\\ &\quad = H_2O + C_4H_3O{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O \qquad (II)\end{aligned}$$

Cette dernière réaction se produit plus ou moins accessoirement avec la réaction (I), et dans des proportions variables, trois molécules d'acétone et une de furfural donnent principalement le dérivé mono-furylique (I), tandis qu'une molécule d'acétone pour deux de furfural donne surtout le dérivé di-furylique (II). Ce fait s'est avéré général pour les cétones étudiées.

Voici le mode opératoire : on met dans un flacon convenable 1/10 molécule-gramme de furfural (9.6 gr.), 3/10 molécules-grammes de cétone grasse et de l'eau (250—500 c.c.).(5) On agite ce mélange jusqu'à dissolution complète. Puis on ajoute 10 gr. de soude caustique à 10 pour 100.(6) Cette solution est ensuite agitée à la machine à secouer pendant 6–7 heures. Après plusieurs minutes on voit qu'elle se trouble, et se teinte légèrement en jaune.

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(1) Voir Partie expérimentale.

(2) Mlle. N. Wolf, loc. cit.

(3) Schmidt, *Ber.*, 14 (1881), 1459.

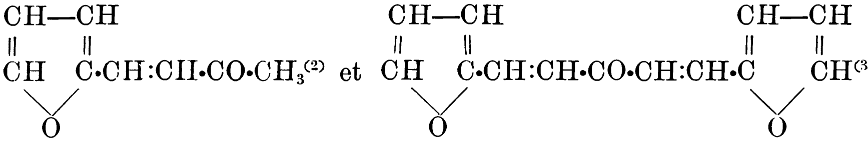
(4) Claisen, *Ber.*, 14 (1881), 2469.

(5) On dose la quantité de l'eau selon la solubilité des cétones, et lorqu'elle est très petite, on ajoute de l'alcool.

(6) Pour éviter la polymérisation du produit de réaction on met souvent de la glace pilée dans le mélange (Ivanoff, loc. cit.), mais dans notre expérience le rendement ne s'est pas amélioré par cette addition.

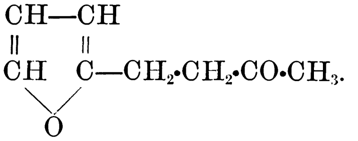
Au bout de la réaction, après avoir ou sans avoir neutralisé la soude en excès, on extrait le corps à l'éther⁽¹⁾, on le lave, et puis on le rectifie sous pression réduite.

1. Furyl-1-butén-1-one-3 et Difuryl-1.5-penta-dién-1.4-one-3,



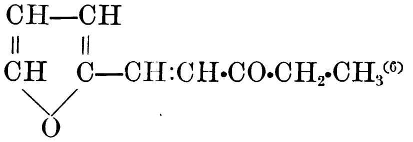
Quand, en les préparant, on varie la proportion de furfural et de cétones, on obtient les rendements aux rapports differants des produit mono- et di-furyliques. On voit au bout de la réaction, que le produit de condensation de deux molécules de furfural et une de cétone, devient bloc dur, duquel on obtient le dérivé di-furylique (rendement, 96 pour 100).

2. Furyl-1-butanone-3,



Ce corps est déjà connu,⁽⁴⁾ et on peut le préparer facilement, en réduisant la buténone correspondante au moyan de l'amalgame de sodium. Nous avons fait quelques mesures : $d_4^{25}=1.026$⁽⁵⁾, $n_D^{25}=1.470$. Réfraction moléculaire : Trouvée, 37.6. Calculée, 37.7.

3. Furyl-1-pentén-1-one-3,



Par la méthode donnée ci-dessus on a obtenu cette cétone non saturée de l'aldéhyde et de la butanone avec rendement 93 pour 100 de théorie. Une huile jaune claire, très réfringente, et bouillant à 90–95° sous 2 mm., à 126° sous 15 mm., et à 234–235° sous pression ordinaire. Elle ne tarde pas à se teindre en rouge brunâtre même à l'abri de la lumière.

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(1) Avant l'extraction, on le distille par une trainée de vapeur d'eau (Schmidt, loc. cit.), mais cette opération est superflue.

(2) Schmidt, loc. cit.; Claisen, loc. cit.

(3) Claisen et Ponder, *Ann. Chem.*, 223 (1884) 146.

(4) Harries et Kaiser, *Ber.*, 32 (1899), 1320.

(5) Harries et Kaiser, $d_4^{19}=1.0361$ (loc. cit.)

(6) La constitution isomérique $C_4H_3O.CH:C(CH_3).CO.CH_3$ est possible. Avec le benzylal et la butanone Harries et Müller ont préparé, sous l'action de l'alcali caustique, un composé de la formule $C_6H_5.CH:CH.CO.CH_2.CH_3$ et, au contraire, sous l'action du chlorure d'hydrogène, une substance isomérique $C_6H_5.CH:C(CH_3).CO.CH_3$ (*Ber.*, 35 (1902), 967. Ici nous admettons *provisoirement* la constitution donnée.

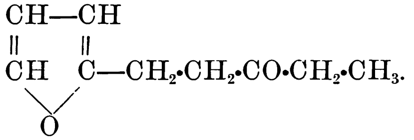
Analyse : Trouvé, C = 72.05, H = 6.36. Calc. pour $C_9H_{10}O_2$, C = 72.00, H = 6.67 %. $d_4^{25} = 1.068$, $n_D^{25} = 1.627$. Réfraction moléculaire : Trouvée, 49.8. Calc., 41.8.

Sémicarbazone :— F = 201.5–202.5° (pas corrigé). Une poudre cristalline, légèrement jaune, de l'alcool.

Analyse : Trouvé, N = 20.8. Calc., pour $C_{10}H_{13}O_2N_3$, N = 20.3 %.

Le dérivé *bisulfitique* ne se forme pas.

4. Furyl-1-pentanone-3,

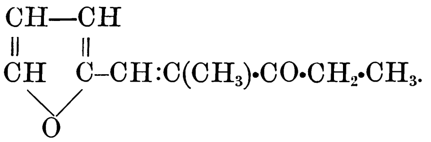


Ce corps, obtenu par réduction de furyl-penténone par l'amalgame de sodium, est une huile assez légère, incolore, bouillant à 206–208° sous pression ordinaire, et à 88° sous 10 mm. Il possède une odeur très agréable.

Analyse : Trouvé, C = 70.8, H = 8.2. Calc. pour $C_9H_{12}O_2$, C = 71.1, H = 7.8 %. $d_4^{25} = 1.003$, $n_D^{25} = 1.468$. Réfraction moléculaire : Trouvée, 42.2 Calc., 42.3.

Ce corps ne se forme pas ni le combinaison *bisulfitique* ni la *sémicarbazone.*

5. Furyl-1-méthyl-2-pentén-1-one-3,

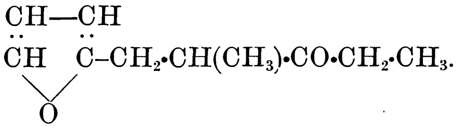


On peut préparer la cétone comme précédemment avec un bon rendement de l'aldéhyde et de la pentanone-3. C'est une huile légèrement jaune, bouillant à 135° sous 12 mm., et se colorant comme les homologues inférieurs.

Analyse : Trouvé, C = 73.0, H = 7.7. Calc. pour $C_{10}H_{12}O_2$, C = 73.2, H = 7.3 %. $d_4^{25} = 1.052$. $n_D^{25} = 1.557$. Réfraction moléculaire : Trouvée, 50.5 Calc., 46.4

Sémicarbazone, poudre blanche, fusible à 175–176°.

6. Furyl-1-méthyl-2-pentanone-3,

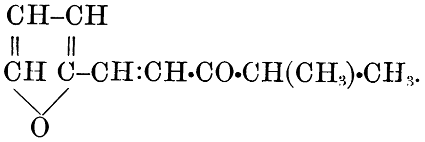


La réduction a été faite comme d'habitude, donnant naissance à cette cétone, huile incolore à odeur fruitée et bouillant à 93–100° sous 13 mm.

Analyse : Trouvé, C = 71.6, H = 8.8. Calc. pour $C_{10}H_{14}O_2$, C = 72.3, H = 8.4 %. $d_4^{25} = 0.995$, $n_D^{25} = 1.466$. Réfraction moléculaire : Trouvée, 46.2. Calc., 46.9

Le dérivé *bisulfitique* ne se forme pas. La *sémicarbazone* n'est pas obtenue à l'état cristallisé.

7. Furyl-1-methyl-4-pentén-1-one-3,



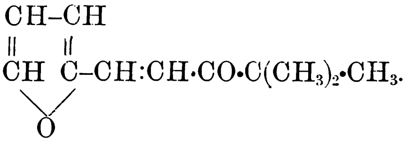
$$\begin{array}{l}\text{CH–CH}\\ \| \quad\; \|\\ \text{CH C–CH:CH}\cdot\text{CO}\cdot\text{CH(CH}_3)\cdot\text{CH}_3.\\ \;\diagdown\diagup\\ \;\;\text{O}\end{array}$$

Le furfural et la méthyl-3-butanone-2$^{(1)}$ donnent cette cétone, huile légèrement colorée en jaune à odeur rappellant celle de l'orange, et bouillant à 133–136' sous 18 mm. Rendement, environ 60 pour 100.

Analyse : Trouvé, C=73.3, H=7.5. Calc. pour $C_{10}H_{12}O_2$, C=73.2, H=7.3 %. $d_4^{25}=1.0199$, $n_D^{25}=1.557$. Réfraction moléculaire : Trouvée, 51.8. Calc., 46.4.

Il ne se forme pas de dérivé *bisulfitique.*

8. Furyl-1-dimethyl-4.4-peutén-1-one-3,



$$\begin{array}{l}\text{CH–CH}\\ \| \quad\; \|\\ \text{CH C–CH:CH}\cdot\text{CO}\cdot\text{C(CH}_3)_2\cdot\text{CH}_3.\\ \;\diagdown\diagup\\ \;\;\text{O}\end{array}$$

Cette substance est obtenue avec l'aldéhyde et la diméthyl-2.2-butanone-3 (pinacoline). On a ajouté de l'alcool au mélange initial pour dissoudre complètement les réactifs. Ce corps condensé est une huile jaune à odeur d'orange, et bout à 145–147° sous 35 mm.

Analyse : Trouvé, C=74.1 H=8.0. Calc. pour $C_{11}H_{14}O_2$, C=74.2, H=7.8 %. $d_4^{25}=1.007$, $n_D^{25}=1.548$. Réfraction moléculaire : Trouvée, 56.9 Calc., 51.1.

Cette cétone ne donne ni le dérivé *bisulfitique* ni la *sémicarbazone.*

9. Préparation catalytique de la diméthyl-2.2-butanone-3 (pinacoline)$^{(2)}$

La transformation du diméthyl-2.3-butane-diol-2.3 en diméthyl-2.2-butanone-3 (pinacone en pinacoline) a été bien étudiée, et en particulier la transformation catalytique en présence de l'alumine par Ipatief$^{(3)}$. Bien que nous n'ayons pas lu son travail original, il nous semble qu'il a fait passé les vapeurs de diol sur de l'alumine maintenue à 300–320'. Nous avons réussi à préparer cette cétone avec un rendement très satisfaisant, en faisant passer les vapeurs de diol$^{(4)}$ sur une trainée de thorine chauffée à 250°. La thorine est préférable à l'alumine, car elle ne s'encrasse pas si vite, et garde son activité plus long temps. Quand elle a perdu l'activité, on peut la recouvrer par simple calcination.

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(1) La méthyl-3-butanone-2 m'a été donnée par mon ami, M. le prof. T. Kusama, que je remercie vivement.

(2) Cette préparation a été faite en collaboration avec M. S. Abe.

(3) P. Sabatier, "La catalyse en chimie organique," 2ème édition (1920), 283.

(4) Ce diol est obtenu par réduction de l'acétone par le magnésium métallique et le chlorure de mercure (Holleman, *Rec. trav. chim.*, 25 (1906), 206. Pour séparer le diol des produits accessoires comme oxyde de mésityle, phorone, etc., on transforme le diol en son hydrate, bien cristallisable, que l'on sépare par essoration de la portion liquide. Par simple distillation du corps hydraté, on obtient le diol à l'état assez pur.

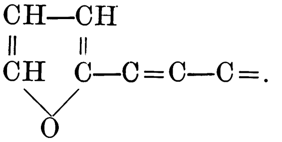
10. Furfural sur camphre.

Le dérivé furfurylique correspondant a été obtenu par Mlle. N. Wolf au moyen de l'amidure de sodium. Nous avons repris ce problème et cherché les conditions de la condensation du furfural avec le camphre (1) au moyen de l'alcali caustique, et (2) aussi par l'éthylate de sodium, comme Semmler et Ascher ont fait son étude sur l'essence de carline[1]. Dans l'un et l'autre des essais nous n'avons pas réussi à condenser les deux réactifs.

11. Quelqurs observations sur les écarts des valeurs trouvées et calculées de la réfraction moléculaire.

Réfraction moléculaire des cétones furyliques.

Substance.	Trouvée.	Calculée.	Ecart.
$C_4H_3O\cdot CH{:}CH\cdot CO\cdot C_2H_5$	49.8	41.8	8.0
$C_4H_3O\cdot CH{:}C(CH_3)\cdot CO\cdot C_2H_5$	50.5	46.4	4.1
$C_4H_3O\cdot CH{:}CH\cdot CO\cdot CH(CH_3)\cdot CH_3$	51.8	46.4	5.4
$C_1H_3O\cdot CH{:}CH\cdot CO\cdot C(CH_3)_2\cdot CH_3$	56.9	51.1	5.8
$C_4H_3O\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$	37.6	37.7	-0.1
$C_4H_3O\cdot CH_2\cdot CH_2\cdot CO\cdot C_2H_5$	42.2	42.3	-0.1
$C_4H_3O\cdot CH_2\cdot CH(CH_3)\cdot CO\cdot C_2H_5$	46.2	46.9	-0.7

La table ci-jointe montre que les écarts des valeurs sont remarquables pour les cétones non sarutées, tandis que pour les corps saturés, ils sont presque négligeables. On rencontre ce même phénomène très souvent parmi les dérivés furyliques[2]. Dans la table on voit que tous les composés furyliques qui présentent ces écarts possèdent sans exception un groupement  Cela tient vraisemblablement à l'existence de deux doubles liaisons conjugées dans les molécules, comme on le voit par ailleurs[3].

Or, par l'étude spectrographique des corps, il nous semble qu'il existe une relation étroite entre l'écartement (l'exaltation) et l'absorption de la lumière, qui sera traitée dans un rapport suivant.

Haute école polytechnique de Yokohama.

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(1) *Ber.*, 42 (1909), 2355. Voir aussi Semmler, *Ber.*, 39 (1906), 726.

(2) D. Ivanoff, loc. cit.; Mlle. N. Wolf, loc. cit.

(3) Le groupement méthyle en position 2 des cétones furyliques produit sur la réfraction moléculaire une diminution de l'écartement. Voir Henrich, "Theorien der organischen Chemie," 5ème édition, (1924), 263.

SYNTHESIS OF METHOXY-HYDROXY-N-METHYL-3·4-DIHYDROISOQUINOLINIUM SALTS.

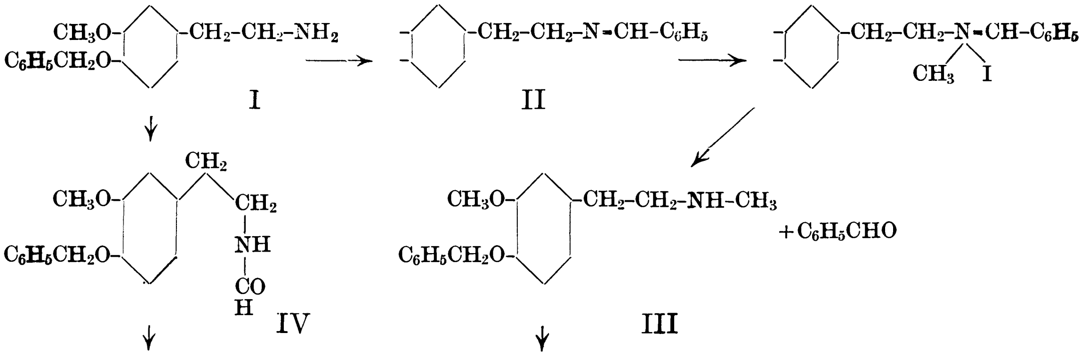
By Shirō AKABORI.

Received April 7, 1926. Published May 28, 1926.

In the dihydroisoquinoline series there are two compounds of much importance from the pharmaceutical point of view. These are hydrastinine and cotarnine, and their hydrochlorides are regarded as having the constitution of 6·7-methylenedioxy-2-methyl-3·4-dihydroisoquinolinium and 6·7-methylenedioxy-8-methoxy-2-methyl-3·4-dihydroisoquinolinium chloride respectively, as is well known. Each of them had first been obtained as an oxidation product of the natural alkaloid hydrastine and of narcotine; later their total synthesis was also successfully achieved.

The present writer has succeeded in preparing several other compounds of this series, namely, 6-methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium and 6-hydroxy-7-methoxy-2-methyl-3·4-dihydroisoquinolinium salts, as well as their benzylethers. The starting substance is β-[3-methoxy-4-benzyloxyphenyl]-ethylamine (I) which has recently been synthesized by S. Kobayashi.(1)

The method of synthesis which was undertaken and applied successfully in the preparation of 6-methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium salt (VIII) is expressed by the scheme below.



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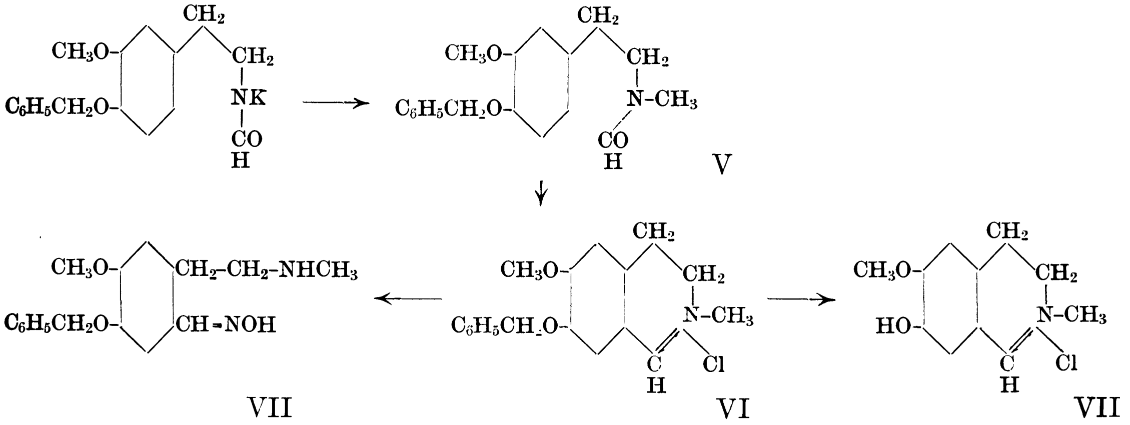
(1) Kobayashi, *Rikagaku Kenkyujo Iho* (in Japanese), **4** (1925), 527.

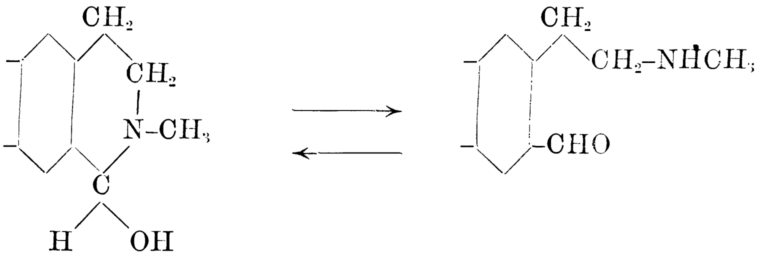


The intra-molecular condensation of formyl-phenyl-ethylamine derivative (V) into dihydroisoquinolinium salt is easily effected by phosphorus oxychloride or thionyl chloride with an exceedingly good yield. Phosphorus pentoxide, however, gives only a poor yield. The most convenient reagent of all is thionyl chloride, for it reacts apparently as follows:—

$$C_{18}H_{21}O_3N + SOCl_2 = C_{18}H_{20}O_2NCl + HCl + SO_2$$

thus directly leading to the formation of the chloride of the expected base. Phosphorus oxychloride, on the other hand, gives the phosphate of the base as an extremely hygroscopic mass, which, therefore, must afterwards be converted into another salt. In spite of the violent evolution of hydrogen chloride at the time of the condensation, the benzyloxyl group remains completely unaffected, while it breaks into benzyl chloride and the free hydroxyl group as a result of the action of concentrated hydrochloric acid.

It is well known that the free bases of hydrastinine and cotarnine react with hydroxylamine to give benzaldoxime derivatives, for they exist in tautomeric forms as below.⁽¹⁾



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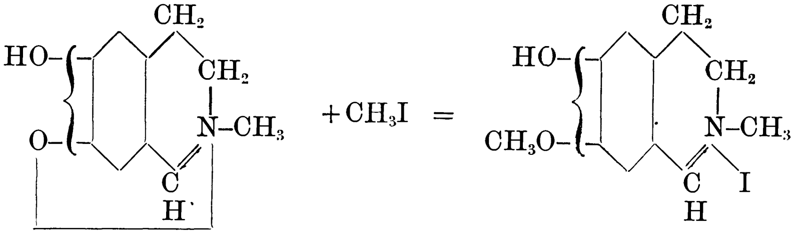
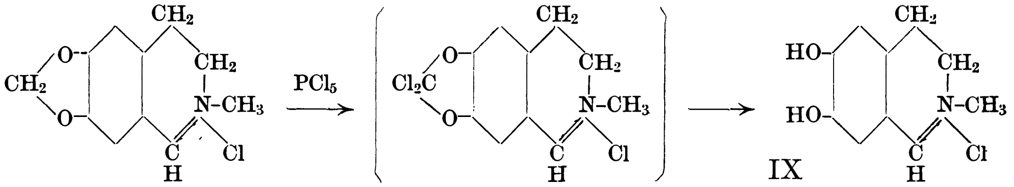
(1) W. Roser, *Ann.*, 249 (1888), 116; 254 (1889), 359.
M. Freund, *Ann.*, 271 (1892), 311; *Ber.*, 22 (1889), 457.
H. Decker, *J. prakt. Chem.*, [2] 47 (1893), 222; *Ber.*, 33 (1900), 2273.
J. Gadamer, *Arch. Pharm.*, 243 (1905), 16.

When treated with hydroxylamine 6-methoxy-7-benzyloxy-2-methyl-3•4-dihydroisoquinolinium salt (VI) is also easily converted into 2-[ω-methylamino-ethyl]-4-methoxy-5-benzyloxy-1-benzaldoxime (VII).

6-Methoxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium salt (VIII) is not a new compound, because it has been obtained by F. L. Pyman⁽¹⁾ by the action of methyl iodide on the phenolbetaine of 6•7-dihydroxy-2-methyl-3•4-dihydroisoquinolinium hydroxide (X). But without making any attempt to establish the relative position of the methoxyl and hydroxyl groups, he expressed the reaction as follows:—



For the purpose of identifying the two substances—Pyman's and the present writer's,—the latter has repeated the former's experiments. 6•7-Dihydroxy-2-methyl-3•4-dihydroisoquinolinium chloride (IX), from which the above mentioned phenolbetaine is readily obtained by treatment with the aqueous solution of sodium carbonate, is prepared by the demethylation of compound VIII, or by the action of phosphorus pentachloride on hydrastinine.



The product of the action of methyl iodide on the phenolbetaine was proved to be absolutely identical with 6-methoxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium iodide, having the same decomposition point. The reaction between methyl iodide and the phenolbetaine may, therefore, be more reasonably expressed as follows:—

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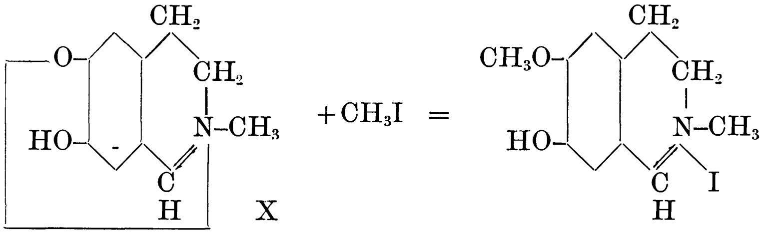
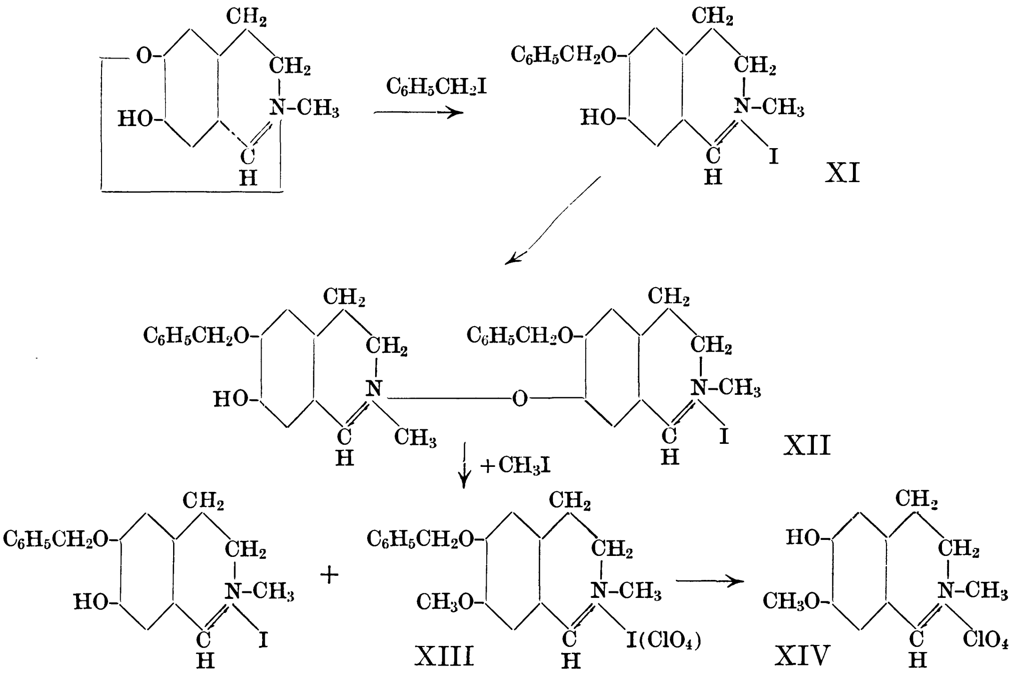
(1) Pyman, *J. Chem. Soc.*, 97 (1910), 268.


X

But the present writer has still some doubt about the constitution of the phenolbetaine.

6-Hydroxy-7-methoxy-2-methyl-3·4-dihydroisoquinolinium salt (XIV), which has the hydroxyl and methoxyl groups in alternate positions as compared with compound VIII, was obtained by the following reactions:—


XI

XII

XIII

XIV

On account of its analogous behaviour, the intermediate compound (XII) is assumed to have a similar constitution to that of Pyman's 6-methoxy-7-[6-methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinoliniumoxy]-2-methyl-3·4-dihydroisoquinolinium chloride.(1) The method of synthesis adopted by the present writer may be available as a general method for the preparation of any compound of the following general type:—

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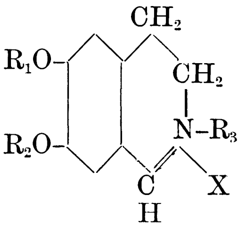
(1) Pyman, *J. Chem. Soc.*, 97 (1910), 269.



Experimental part.

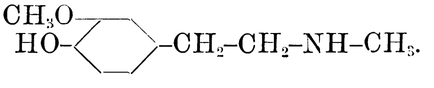
Methyl-β-[3-methoxy-4-benzyloxy-phenyl]-ethylamine, (III). The synthesis of this new base was carried out according to the method, which H. Decker and P. Becker(1) employed in their synthesis of methyl-homo-piperonylamine from homo-piperonylamine. β-[3-methoxy-4-benzyloxy-phenyl]-ethylamine and benzaldehyde, brought together in molecular proportion, react, under spontaneous heating, to give benzal-β-[3-methoxy-4-benzyloxy-phenyl-ethylamine (II). This was purified by recrystallization from a mixture of benzene and petroleum ether; m.p. 57–59°. It crystallizes in light yellow leaflets having a silky lustre.

0.1464 gr. subst. gave 0.4298 gr. CO_2 and 0.0849 gr. H_2O. (Found: C=80.07; H=6.49. $C_{23}H_{23}O_2N$ requires C=79.96; H=6.72%).

The benzal-derivative gives iodemethylate on being heated for about half an hour at 50–60° with methyl iodide in a reflux apparatus perfectly protected from moisture. The iodemethylate is readily hydrolysed in moist alcohol into methyl-β-[3-methoxy-4-benzyloxy-phenyl]-ethylamine hydroiodide and benzaldehyde. The hydrochloride was obtained by passing dry hydrogen chloride into an ethereal solution of the free base. This hydrochloride is easily soluble in water, but moderately so in alcohol, from which it crystallizes in large prisms; m.p. 157–158°. Yield 80%.

0.1303 gr. subst. gave 0.0597 gr. AgCl. 0.1326 gr. subst. gave 0.3213 gr. CO_2 and 0.0844 gr. H_2O. (Found: C=66.08; H=7.12; Cl=11.33. $C_{17}H_{21}O_2N{\cdot}HCl$ requires C=66.31; H=7.21; Cl=11.53%).

The picrate crystallizes in yellow needles from alcohol; m.p. 163.5–165°. The free base boils under reduced pressure without decomposition; b.p. 200–202° (3.5 mm.)



Methyl-homo-vanillylamine, $(CH_3O)(HO)C_6H_3\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_3$. This amine plays no part in the course of the synthesis, but is somewhat interesting in constitution being closely related to adrenaline. The hydrochloride

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(1) Decker u. Becker, *Ann.*, 395 (1913), 336.

was obtained by the action of concentrated hydrochloric acid on methyl-β-[3-methoxy-4-benzyloxy-phenyl]-ethylamine; m.p. 149.5–151°.

0.1011 gr. subst. gave 0.0684 gr. AgCl. 10.08 mg. subst. gave 0.540 c.c. nitrogen (11.5°, 756.5 mm.) (Found: Cl=16.74; N=6.40. $C_{10}H_{15}O_2N \cdot HCl$ requires Cl=16.30; N=6.44%).

Formyl-methyl-β-[3-methoxy-4-benzyloxy-phenyl]-ethylamine, (V). 3.2 grams of formate of methyl-β-[3-methoxy-4-benzyloxy-phenyl]-ethylamine (m.p. 105–106°) were heated for half an hour at 170–175°. The product was dissolved in benzene, washed with dilute hydrochloric acid, and subsequently with dilute alkali. After expelling the greater part of the solvent some light petroleum was added. When it had been left standing overnight the formyl-derivative was deposited as a white crystalline mass. This was purified by recrystallization from 50% alcohol, from which it separated in white prismatic crystals; m.p. 78–80°. Yield 2.7 gr. The same compound was also obtained from formyl-β-[3-methoxy-4-benzyloxy-phenyl]-ethylamine (IV m.p. 69–71°) by treatment first with metallic potassium and then with methyl iodide according to D.R.P. 332,474. Yield 90%. This formyl-derivative is readily soluble in ordinary organic media, but insoluble in water.

0.1245 gr. subst. gave 0.3287 gr. CO_2 and 0.0835 gr. H_2O. (Found: C=72.01; H=7.51. $C_{18}H_{21}O_3N$ requires C=72.20; H=6.92%).

6-Methoxy-7-benzyloxy-2-methyl-3·4-dihydroisoquinolinium salts, (VI). 4 grams of the above mentioned compound (V) were dissolved in 20 c.c. of toluene, to which 4 grams of thionyl chloride were added. On being gently heated, the clear mixture became turbid, and then followed a copious evolution of gas, the reaction being complete after a few minutes. The resinous mass, which was deposited at the bottom of the vessel, was separated from the supernatant liquid and washed with light petroleum (during this operation the resinous mass gradually became crystalline), and finally recrystallised from a mixture of alcohol and acetone. This chloride crystallizes in two forms,—one light yellow, short prisms, which melt at 135–138°, after sintering at 125°, the other colourless, large prisms, which melt gradually between 70° and 120°. After being dried in a vacuum at 80°, both of them melt at 135–138° and effervesce at 142°. The aqueous solution of this compound exhibits, in a marked degree, the property of fluorescence, and has a strong bitter taste. These properties are exactly similar to those of hydrastinine. Moreover, in a single qualitative test of its physiological behaviour, it contracted the uterus muscle of a rat.

Yellow sample—0.1078 gr. subst. became 0.1023 gr. after being dried in a vacuum at 80°, and gave 0.0443 gr. AgCl. (Found: H_2O=5.10; Cl=10.17. $C_{18}H_{20}O_2NCl \cdot H_2O$ requires H_2O=5.37; Cl=10.54%).

Colourless sample—0.1644 gr. subst. became 0.1477 gr. after being dried in a vacuum at 80°. (Found: $H_2O=10.16$. $C_{18}H_{20}O_2NCl\cdot 2H_2O$ requires $H_2O=10.19\%$).

Anhydrous sample—0.1082 gr. subst. gave 0.2704 gr. CO_2 and 0.0592 gr. H_2O. (Found: C=68.16; H=6.12. $C_{18}H_{20}O_2NCl$ requires C=68.01; H=6.35%).

The picrate crystallizes in golden-yellow plates, which melt at 177–178°.

5.56 mg. subst. gave 0.505 c.c. nitrogen (9.2°, 762.5 mm.) (Found: N=11.05. $C_{24}H_{22}O_9N_4$ requires N=10.98%).

2-[ω-methylamino-ethyl]-4-methoxy-5-benzyloxy-1-benzaldoxime, (VII). 1 gram of 6-methoxy-7-benzyloxy-2-methyl-3·4-dihydroisoquinolinium chloride was dissolved in 10 c.c. of water, to which was added 0.3 gram of hydroxylamine hydrochloride in 5 c.c. of water, and the solution was then made alkaline with sodium carbonate. The whole was slightly warmed on a water bath, when the white crystalline oxime was deposited almost quantitatively. A pure sample, recrystallized from alcohol, melts at 166–167°. It turns red on exposure to the daylight.

0.1081 gr. subst. gave 0.2713 gr. CO_2 and 0.0647 gr. H_2O. (Found: C=68.46; H=6.70. $C_{18}H_{22}O_3N_2$ requires C=68.78; H=7.06%).

(To be continued.)

STUDIES ON PROTEINS. II.(1)

ACTION OF SUPERHEATED WATER ON PROTEINS. I.

By **Shigeru KOMATSU** and **Chuichi OKINAKA.**

Received April 7, 1926. Published May 28, 1926.

Taylor(2) has observed that when pure sterile globulin from bovine serum was kept in distilled water at ordinary temperature for 18 months, it was hydrolysed to proteoses and partly polymerised into an insoluble form, and also that leucine may be recovered from a sterile suspension of casein in pure water after the lapse of a year or more. These facts indicate that the hydrolysis of proteins in neutral aqueous solution does occur at ordinary temperature, though the velocity of the autohydrolysis of proteins was very slow under these conditions. The influence of heat upon the autohydrolysis of proteins is of considerable interest, since it was a generally accepted view

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(1) The first report has been published in *The Journal of Biochemistry,* 2 (1922), 365.

(2) *J. Biol. Chem.,* 1 (1906), 345; "On Fermentation," (1907), p. 223.

that the reaction of hydrolysis is accompanied by the evolution of heat and that the heat-coagulation of proteins was considered to consist in the polymerisation of the amphoteric proteins molecule with the elimination of water according to the following equation :

$$H{\cdot}X{\cdot}OH + H{\cdot}X{\cdot}OH = H{\cdot}X{\cdot}X{\cdot}OH + H_2O$$

and accordingly, the effect of applying heat to a protein solution must be to shift the equilibrium in the direction of polymerisation, as would follow from van't Hoff's law(1).

The study of the action of superheated water on proteins was first tried by Wöhler(2), and his report was followed by contributions from Subanin(3), Lubavin(4) and others(5) on the isolation of cleavage products of proteins.

The net result of these researches was (1) to establish that the protein body suffers fairly complete hydrolysis at the temperature of steam, and that the equilibrium between the protein-complex and the amino acids, which were regarded as the products of its hydrolysis, was shifted to the amino acids side ; (2) to show the presence of leucine, tyrosine, aspartic acid and atmidbodies of complex nature in the reaction products of the proteins.

The extensive researches by R. Neumeister(6), and R.H. Chittenden and F.S. Meara(7) have given us much additional informations concerning the mode of cleavage of the protein molecule, though there are different opinions regarding the nature of the process which have revealed an important connection with the hydrolytic process brought about by the digestive enzymes and also by dilute acids. Many investigators mentioned above, have contented merely to examine the products, especially from the view point of physiology, to find some analogies between the action of superheated water and gastric or pancreatic digestion. Such a too close adherance to

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(1) Robertson, "The Protein," (1909), pp. 141 and 173.

(2) *Lieb. Ann.*, 41 (1842), 238.

(3) Hoppe-Seyler, "Medicin-chem. Untersuch.", (1871), p. 480.

(4) *Ber.*, 10 (1877), 2237.

(5) Hammersten, *Z. physiol Chem.*, 7 (1883), 227.
Krukenberg, *Sitzungsber. der Jenaischen Gesell. für Medicin, etc.* (1886).
A. Clermont, *Compt. rend.*, 105 (1887), 222.
Crismer, *Jahres Berichte f. Thiechemie für 1891*, 19.
Koukol-Yasnopolsky, *Pflüg. Arch. Physiol.*, 12, 85.
R. Neumeister, *Z. Biol.*, 26 (1890), 57; 36 (1898), 420.
E. Salkowski, *Z. Biol.*, 34 (1896), 190; 37 (1899), 404.
R.H. Chittenden and F.S. Meara, *J. physiol.*, 15 (1896), 501.
Blum u. Vaubel, *J. prakt. Chem.*, 56 (1897), 396; 57 (1898), 365.
R. Bauer, *Z. physiol. Chem.*, 35 (1902), 342.
H.S. Steudel, *Z. physiol. Chem.*, 35 (1902), 540.

(6) Loc. cit.

(7) Loc. cit.

analogies might lead investigators into serious error as was already pointed out by Chittenden and Meara, and cause them to fail to pay attention to the unraveling of the constitution of proteins. Furthermore, it was doubtful whether the atmid-bodies would result in a definite chemical composition, in spite of the intensity and duration of heating by which they were produced.

Nobody paid any attention to the formation of the insoluble substance from proteins by the action of superheated water, nor offered any explanation of its relation to the atmid-bodies, all merely dwelling on the constitution of the latter substances. The present research, to heat proteins with water in the iso-electric point, therefore, was undertaken by the authors, to find some chemical relation between the insoluble substance and the atmid-bodies, to propose chemical constitution of protein, if possible, and also to explain the mechanism of the decomposition of protein by superheated water.

The materials employed in the present experiment were three different proteins; edestin, gliadin from wheat flour, and casein from cow's milk, which were prepared by the authors following the directions proposed by T. B. Osborne and his coworkers(1). The results of the analysis of the samples are shown in the following table:

TABLE 1.

	Edestin	Gliadin	Casein
C.	51.3	53.78	53.39
H.	6.86	6.79	9.10
N.	18.63	17.65	15.55
Ash.	0.7	0.5	0.25
H_2O	6.43	4.1	3.67
Amide-N.	1.88	4.30	1.61
Monoamino-N	10.87	12.25	10.31
Diamino-N.	5.9	1.09	3.49
Melanin-N.	0.12	0.14	0.21
P_H(2)	6.3	5–6 (mean 5.7)	4.6

One gram of protein was introduced with 20 c.c. of distilled water into a glass stoppered bottle of 70 c.c. capacity which was previously washed with steam in order to remove completely any alkaline substance

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(1) *J. Am. Chem. Soc.*, 25 (1903), 323.

(2) P_H of the pure protein was determined by the electrometric method of the solution which was prepared by shaking the protein with distilled water in a stoppered bottle for 24 hours. According to Michaelis, the P_H for edestin and for casein is 5.6 and 4.7 respectively, and Eto (*J. Biochem.*, 3 (1924), 373) have given 6.6 for that of gliadin.

which might be generated from the glass wall by the action of steam. The bottle was carefully stoppered, and heated in a thermostat which was kept at the constant temperature of 110° and 120°. The bottle was opened after heating for a certain number of hours, and the fluid which had generally an yellow colour, and gave a neutral reaction to litmus paper, was poured into a flask. The insoluble residue separated from the coloured solution, was washed with cold water, and then dried to constant weight at 105°. The solution and washings combined together, made up to 50 c.c., and the P_H value of the solution was determined electrometrically using one part of the solution. Another part of the solution was evaporated on a water bath to dryness and dried at 110° to constant weight and then analysed.

The elementary composition and the distribution of nitrogen of both the insoluble residue and the solution were determind in the usual way, and the results are shown in Table 2 and Table 3.

The constituents of the hydrolysate of protein by the action of superheated water can be divided, according to their solubilities in water, into two parts; the insoluble residue, and the soluble substances, and the latter composed of a substance of complex nature such as proteose, and of simple amino acids, and the quantity of the soluble substances as was indicated in Table 2, was increased in proportion to the reaction time. The rate of dissolution of protein in water, being different for individual protein, is greatest in edestin, and gliadin and casein were ranged in that order.

The total weight of the hydrolysate as will be seen in Table 2, exceeded in all cases the employed amount of the sample, indicating the hydrolysis of protein molecule occurred in the digestion.

Although the insoluble residue has the same appearance as the mother protein, they are different essentially in composition from each other, as indicated in Table 3, the insoluble residue resulting from edestin is rich in the content of carbon and hydrogen than the mother protein, while that from gliadin is poor in carbon but rich in hydrogen, and the insoluble substance derived from casein is rich in carbon but poor in hydrogen compared with the mother protein.

Generally, the insoluble substance has no definite chemical composition which varying with the external conditions under which the protein was submitted to the chemical action; the substance derived from edestin shows gradual increase in carbon and hydrogen-content with lapse of the reaction time, while that from casein and gliadin keep almost constant value.

These facts led the authors to the conviction that the chemical composition of the detached groups from protein should vary with each individual protein according to the amino acids of which it was composed⑴.

Moreover, the study of the nitrogen distribution of the insoluble and soluble parts by the usual methods, supports the above idea with regard to the composition of the hydrolytic products, and also suggests the formulation of an hypothesis with respect to the nature of the process in which protein undergoes hydrolysis.

When edestin was digested, the groups containing amide nitrogen were removed from the protein molecule mostly at the beginning of the reaction, whilst those containning diamino nitrogen were detached gradually, and consequently the hydrolysis of the protein proceeded in a manner in which the distribution of nitrogen in the residue and solution will approach, in the progress of reaction, that in the original protein. Casein, however, shows quite different behavior toward super heated water, since the atomic groups containing diamino-nitrogen were removed mostly from the protein molecule at the first period of the reaction, and gliadin with respect to its behavior stands between these two proteins.

TABLE, 2.

			Casein (120°)			Gliadin (120°)			Edestin (110°)		
		Heating (hrs.)	2	6	17	2	6	15.5	3	6	9
		Sample (gr.)	0.8998	0.9740	0.9672	0.9749	0.9880	1.0028	0.9200	0.9200	0.9200
		Solution (gr.)	0.012	0.057	0.14	0.054	0.097	0.289	0.134	0.212	0.310
		„ (%)	1.34	5.85	14.00	5.5	9.9	28.8	14.3	22.6	33.0
		Residue (gr.)	0.9228	0.9331	0.8365	—	0.9414	0.7265	0.8986	0.8678	0.6330
		„ (%)	102.6	95.8	86.5	—	96.2	92.4	97.7	94.3	74.2
Distribution of N.	Solution.	Total N. (%)	—	17.0	15.0	16.3	14.4	16.2	16.2	18.7	17.8
		Amide N. (%)	—	4.5	2.6	—	4.6	5.0	3.0	3.4	2.7
		Diam. N. (%)	—	3.3	2.0	—	0.7	0.8	3.7	4.4	4.7
	Residue.	Total N. (%)	16.0	15.3	15.5	—	15.2	23.1	16.9	16.2	18.3
		Amide N. (%)	—	1.3	2.1	—	4.9	6.9	1.6	1.3	1.4
		Diam. N. (%)	—	3.0	5.1	—	0.8	1.5	5.4	4.9	5.3

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(1) G. Trier, "Chemie der Pflanzenstoffe," (1924), p. 470.
O. Cohnheim, "Chemie der Eiweisskörper," 3 Aufl. (1911), p. 279.

TABLE, 3.

Elementary Analysis of Residue and PH of the Solution.

	Edestin (120°)			Gliadine (120°)			Casein (120°)		
Heating (hrs.)	Carbon	Hydrogen	PH	Carbon	Hydrogen	PH	Carbon	Hydrogen	PH
0	51.36	6.86	6.3	53.87	6.79	5.7	53.39	9.13	4.6
1	51.80	7.55	7.3			—			—
6			—	52.27	7.11	6.8	54.29	7.34	4.7
20	52.46	7.20	6.9	52.19	6.85	6.4	54.27	7.17	5.0

It was a noteworthy fact that the total amide nitrogen of the reaction products at the various stages of the reaction, as will be seen in the case of edestin heated with water at 110°, exceeded that of the protein, and on the contrary there shows a corresponding diminution in the total diamino-nitrogen of the reaction products when compared with the original sample. These facts indicate the transformation of the diamino-nitrogen into amide-nitrogen, and also the phenomenon was noticed markedly in the case of casein, but in gliadin the reaction takes place in the least degree.

Such conversion of nitrogen compounds seems to be more probable when referred to the transformation of glyoxalin by the action of benzoyl chloride and alkali at 0° into bis-benzoyl amino ethylene(1), and also the behavior of tryptophane towards chemicals(2). Consequently, the process involved in the appearance of the insoluble residue by the action of super-heated water on protein was regarded as taking place in at least two ways.

First, there is a formation of an insoluble substance resulting by the removal of the prominent parts from the protein complex. Second, one part of other cleavage products soluble in water, formed simultaneously, was subsequently converted to another insoluble substance by the condensation. The remainder of the soluble substances exists with amino acids side by side in the solution, does or does not change its chemical structure.

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(1) Bamberger and Berle, *Lieb. Ann.*, 273 (1893), 351.

(2) Hoppe-Seyler, "Physiol.-Pathol. Chem. Analyse," 9 Aufl. (1924), p. 315.
A. Kossel u. S. Edlbacher, *Z. physiol. Chem.*, 93 (1915), 396.
A. Windaus, *Ber.*, 43 (1910), 499.

The study of the P_H value of the individual reaction products and also their buffer action will be of some important service for the verification of the hypothesis with regard to the chemical reactions above mentioned, and the results will be described in detail in the next article.

October 1924.

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A SIMPLE MANOMETER FOR MEASURING LOW PRESSURES(1)

By Toshiaki SHIRAI.

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According to the kinetic theory of gas, the heat conductivity of a gas is independent of its pressure. This fact was verified experimentally by observing the cooling velocity of a body which is kept in the gas. Thus the time which is required to cool from a given temperature to another under a constant condition, is independent of the pressure of the surrounding gas. But this rule holds only within a limited range of pressures. Under high pressures it is disturbed by the convection of gas and by other phenomena. And at the pressures lower than few millimetres of mercury, longer time is required for the cooling of the same temperature range under the same condition. This fact was first observed by Kundt and Warburg,(2), and was attributed to the discontinuity of the temperature gradient, which grows prominent at the boundary of the solid and gas, as the pressure diminishes.

Such a behavior of rarefied gas is sometimes utilised as the measure of its pressure. Pirani's manometer(3) and Rohn's manometer(4) belong to this type. Since then many improvements were reported(5). The manometers of this type do not directry show the pressure, as Mc Leod manometer does, so we must calibrate them with known pressures. They are, however, free from mercury vapour, the existence of which will prevent the correct reading of the pressure, and moreover proves to be a hindrance to the perfect evacuation. Another great defect of Mc Leod manometer is that it cannot be used to measure the pressures of easily condensible vapours. For these reasons, in many cases, more complicated manometers such as those described above are used in place of the Mc Leod manometer.

Experimental. Here we describe another substitute for Mc Leod manometer, which is more simple and far less expensive than all other manometers. The construction of it is shown by *M* in Fig. 1. A thermometer

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(1) Read before the Chemical Society of Japan, April, 1924.

(2) Kundt and Warburg, *Pogg. Ann.*, **156** (1875), 177.

(3) Pirani, *Verh, d. D. Phys. Ges.*, **8** (1906), 686.

(4) Rohn, *Z. Electrochem., Sec.*, **20** (1914), 534.

(5) Hale, *Trans. Amer. Electrochem., Soc.*, **20** (1911), 234.
Sô, *Proc. Tokyo Math. Phys. Soc., 3rd. Series*, **1** (1919), 152.
Campbell, *Proc. Phys. Soc. Landon*, **33** (1921), 287.

is fixed in a tube, which is specially so constructed that it has long cylindrical mercury bulb, and graduated to indicate one tenth of a degree. The thermometer should not be deformed by pressure change, and it is more prefarable that it is as sensitive as possible. These two contradictory requirements considerably restrict the sensitiveness of this manometer.

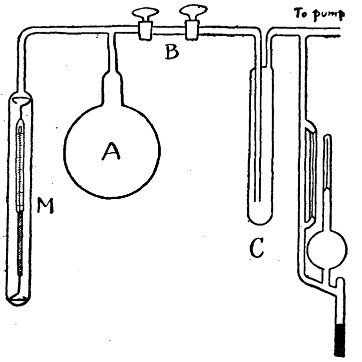

Fig. 1.

Now this apparatus, as already described, must be calibrated with known pressures. The pressures below to few tenth of a millimetre were compared with a Mc Leod manometer. For the pressures lower than these, a pipette system has been used which is shown in Fig. 1. The volumes of the spaces $M+A$ and B are known. At first the spaces A, B and M were thoroughly evacuated and then charge B with a gas of known pressure, and let it expand into A, M and B. As these volumes are known we can easily calculate the pressure after expansion of the gas. During evacuation the mercury trap C is cooled by liquid air to prevent the invasion of mercury vapour into the system. At a known pressure, the cooling velocity of the thermometer is measured by the following manner.

At first, M is warmed, and then suddenly envelop it with a bath of lower constant temperature. Now the thermometer begins to cool, and the time required to cool from a given temperature to the other is measured. It may be convenient to choose 0°, of melting ice, for the temperature of the bath. But in the present experiment, as the graduation of thermometer was from 30° to 42°, the cooling bath of 25° was used, and measured the time required to cool the thermometer from 39° to 32°. Limiting the range of the operating temperature narrower, we can well express the cooling velocity with the Newton's law of cooling, consequently we can easily calculate the requiring time even when we failed to measure the time of cooling for the given temperature range or when the thermostat was not exactly fixed at 25°. The Newton's law is

$$-\frac{dT}{dt} = k'(T-T_0), \quad \cdots\cdots (1)$$

or

$$t = k' \log \frac{T_1-T_0}{T_2-T_0}, \quad \cdots\cdots (2)$$

where t is the time required to cool from a temperature T_1 to another temperature T_2, T_0 is the temperature of the bath and k' is a constant depending on the pressure.

The cooling times obtained under various pressures are plotted against pressure in Fig. 2. As each gas has its own heat conductivity, different curves are obtained for different gases. The curves given are those for air and hydrogen.

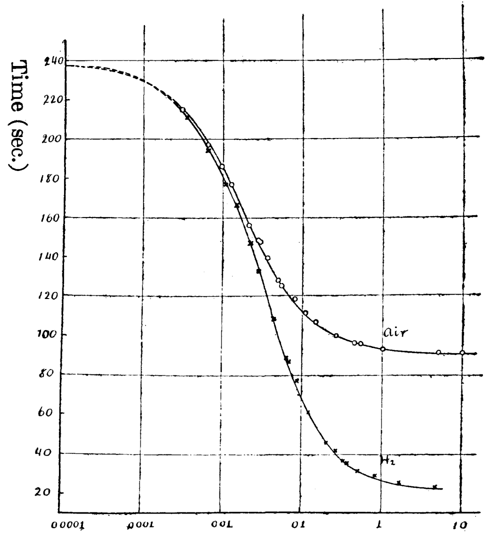

Fig. 2. Pressure (mm. in log. scale)

If such curves were drawn for an apparatus, we can use it as a manometer. Now to construct these curves we must make troublesome measurements. But as is shown in the following pages, if we use a thermometer of long cylindrical mercury bulb, and limit the operating temperature range narrow enough, this pressure-time relation can be expressed in the following form:

$$p = k\,\frac{t_0-t}{t-t_{760}}\text{.....................}(3)$$

where t is the cooling time when the pressure is p, t_0 and t_{760} are the cooling times for the highest vacuum

Air			Hydrogen		
p mm.	t sec.	$k = p\frac{t-t_{760}}{t_0-t}$	p mm.	t sec.	$k = p\frac{t-t_{760}}{t_0-t}$
760.	90.5 ($=t_{760}$)		770.	20.9 ($=t_{760}$)	
250.	90.5		223.	20.9	
26.	90.5		50.	21.0	
15.5	90.6		18.	21.3	
5.0	90.9		5.0	22.6	
1.8	91.0		1.62	25.1	
1.01	92.8		0.78	29.0	0.0295
0.52	95.5	0.0183	0.55	31.8	0.0291
0.43	95.9	0.0172	0.382	36.3	0.0292
0.262	100.0	0.0181	0.380	36.7	0.0299
0.145	107.2	0.0169	0.265	42.6	0.0296
0.108	110.7	0.0171	0.222	41.5	0.0285
0.0809	118.0	0.0186	0.124	61.0	0.0282
0.0540	124.2	0.0160	0.0860	76.5	0.0296
0.050	127.7	0.0186	0.0660	85.8	0.0285
0.0375	139.0	0.0185	0.0645	87.3	0.0286
0.0280	147.5	0.0177	0.0430	108.2	0.0290
0.0270	148.0	0.0173	0.0271	132.9	0.0290
0.0212	156.0	0.0171	0.0215	140.9	0.0267
0.0124	177.0	0.0177	0.0143	165.3	0.0285
0.00934	185.7	0.0172	0.0106	177.0	0.0274
0.00623	197.4	0.0166	0.00714	194.1	0.0285
0.00312	210.0	0.0133	0.00357	210.9	0.0255
0.0000	237.5 ($= t_0$)	—	0.0000	237.5 ($=t_0$)	—
		mean 0.01759			mean 0.02874

and 760 mm. respectively and k is a constant depending upon the nature of the gas and the dimentions of the apparatus. The experimental results are shown in the above table, together the values of k calculated therefrom. The curves in Fig. 2 represent these results.

Theoretical. Smoluchowski⁽¹⁾ introduced a quantity γ under the name of "Temperatursprungskoeffizient", having the following relation,

$$T' - T = \gamma \frac{\partial T'}{\partial n} \cdots\cdots\cdots\cdots (4)$$

where T is the temperature of the solid at the boundary, T' is that of the gas contacting to it, n is a normal drawn at the boundary surface inwards to the gaseous space, and γ is a proportionality constant. He has known experimentally that the quantity γ is proportional to the mean free path of the gas. Now, as the mean free path is inversely proportional to the pressure p, we can express this relation as follows,

$$\gamma p = \text{constant} \cdots\cdots\cdots\cdots (5)$$

This shows that if p decreases γ becomes larger, consequently $T' - T$ becomes larger and $\frac{\partial T}{\partial n}$ smaller. Under the pressures higher than few millimetres γ is negligibly small, so we cannot find any difference botween T and T', and there exists no cause that prevents the heat transmission through the boundary.

Assuming that the cylindrical mercury bulb of radius r_1, and the outer tube of radius r_2 are coaxial, and moreover we consider another coaxial cylinder between them, whose radius is r. Then, as the bulb is long, we may assume that there is no heat loss from the ends of the bulb. The heat transmission at the side of cylinder takes place in two ways, a part by conduction, which depends upon the conductivity of the gas $\varkappa$. temperature gradient $(\partial T'/\partial r)$ at this point, and the surface area of this cylinder $2\pi rl$, the other part by radiation, which can be regarded to be propartional to the difference of the temperature of the thermometer and that to the bath $(T - T_0)$, when the range of the operating temperature is narrow, otherwiese it obeys Stefan-Boltzmann's law.

Now in a unit time the thermometer bulb will lose the heat quantity $-C\frac{dT}{dt}$, so the following relation will be obtained;

$$-C\frac{dT}{dt} = -\varkappa \frac{\partial T'}{\partial r} 2\pi rl + A'(T - T_0) \cdots\cdots\cdots\cdots (6)$$

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(1) Smoluchowski, *Ann. d. Phys. u. Chem.*, **64** (1898), 101.

Comparing (6) with (1), we obtain,

$$-\frac{dT}{dt} = (B+A')(T-T_0) \cdots\cdots\cdots\cdots (7)$$

where $A' = -\frac{A}{C}$, $B = -\kappa 2\pi r l \frac{\partial T'}{\partial r} \frac{1}{C} \frac{1}{T-T_0}$, and $k' = B+A'$.

As κ, π, l, T_0 and C are constants, moreover T is constant at a moment, $\frac{\partial T'}{\partial r} r$ must also be constant at the moment, or

$$r\frac{\partial T'}{\partial r} = a \cdots\cdots\cdots\cdots (8)$$

This expression shows the distribution of temperatures of the gas from r_1 to r_2 at that moment; and the difference of the temperatures at r_1 and r_2 is given by

$$T'_{r_1} - T_{r_2} = a \log \frac{r_1}{r_2} \cdots\cdots\cdots\cdots (9)$$

From the relation (4)

$$\left.\begin{aligned} T'_{r_1} - T &= \gamma\left(\frac{\partial T'}{\partial r}\right)_{r_1} \\ T'_{r_2} - T_0 &= -\gamma\left(\frac{\partial T'}{\partial r}\right)_{r_2} \end{aligned}\right\} \cdots\cdots\cdots\cdots (10)$$

Comparing these with (8), we get

$$\frac{T'_{r_1} - T}{\gamma} r_1 = \frac{T_0 - T'_{r_2}}{\gamma} r_2 = a$$

or

$$\left.\begin{aligned} T'_{r_1} - T &= a\gamma \frac{1}{r_1} \\ T_0 - T'_{r_2} &= a\gamma \frac{1}{r_2} \end{aligned}\right\} \cdots\cdots\cdots\cdots (11)$$

From (9) and (11) we obtain,

$$T_0 - T - a \log \frac{r_1}{r_2} = a\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

or

$$a = \frac{T_0 - T}{\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \log \frac{r_1}{r_2}} \cdots\cdots\cdots\cdots (12)$$

Then

$$B = -\frac{\kappa 2\pi l}{C} \frac{1}{\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \log \frac{r_1}{r_2}} \cdots\cdots\cdots\cdots (13)$$

By equation (5), this can be written in the form :

$$B = \frac{1}{\dfrac{a}{p} + b} \quad \cdots\cdots\cdots\cdots (14)$$

where $a = \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \frac{C}{2\pi l} \times \text{constant}$, and $b = \log \frac{r_1}{r_2} \frac{C}{\varkappa 2\pi l}$.

Now the integral form of (7) is

$$\log \frac{T_1' - T_0}{T_2' - T_0} = (B + A')\, t \quad \cdots\cdots\cdots\cdots (15)$$

In the perfect vacuum no conduction takes place, so $B = 0$, therefore

$$\log \frac{T_1' - T_0}{T_2' - T_0} = A'\, t_0 \quad \cdots\cdots\cdots\cdots (16)$$

From (14), (15) and (16) we obtain,

$$\left(\frac{1}{t} - \frac{1}{t_0}\right) A'\, t = \frac{1}{\dfrac{a}{p} + b} \quad \cdots\cdots\cdots\cdots (17)$$

If p is larger than few millimetres of mercury, then the value of a/p may be neglected to b, and the following relation will be obtained,

$$\left(\frac{1}{t_{760}} - \frac{1}{t_0}\right) A'\, t = \frac{1}{b} \quad \cdots\cdots\cdots\cdots (18)$$

Substituting the value of b from (18) to (17),

$$\frac{1}{\left(\dfrac{1}{t} - \dfrac{1}{t_0}\right) A'\, t_0} = \frac{a}{p} \cdot \frac{1}{\left(\dfrac{1}{t_{760}} - \dfrac{1}{t_0}\right) A'\, t_0}$$

or

$$\frac{a}{p} A' = \frac{t_0}{t_0 - t_{760}} \frac{t - t_{760}}{t_0 - t}$$

Putting

$$k = \frac{t_0 - t_{760}}{t_0} a . A'$$

in the above equation, we obtain the relation (3),

$$p = k \frac{t_0 - t}{t - t_{760}}.$$

Summary.

A simple all glass manometer, which can be used for measuring the pressures from 0.1 mm. to 0.001 mm. has been described. The manometer

consists of a thermometer enclosed in a tube. The pressure measurement is done by measuring the time required to cool the thermometer from a given temperature to the other under a given condition. Using a thermometer of long mercury bulb and limiting the operating temperature range so narrow that the Newton's law of cooling holds, we get the following relation :

$$p = k\frac{t_0 - t}{t - t_{760}}.$$

This relation was well confirmed by experiments using the air and the hydrogen.

In conclusion I wish to express my hearty thanks to Prof. J. Sameshima, under whose guidance the present investigation was carried out.

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ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. III.

By San-ichiro MIZUSHIMA.

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With the electric wave of 9.5 metres, the measurements were carried out as the continuation of previous experiments.(1) The results obtained for monovalent alcohols are shown in the following tables.

ΔC : Displacement of glass plate,
$\Delta C'$: Corrected value of ΔC,
I/I_0 : Ratio of the deflections of the galvanometer at resonance,
ε : Dielectric constants,
K: Electric conductivity which is equivalent to anomalous absorption (cm^{-1} ohm^{-1}).

References : L.—Landolt u. Jahn, *Z. physik. Chem.* 10 (1892), 289.
A.—Abegg, *Wied. Ann.*, 60 (1897), 54.
A.S.—Abegg u. Seitz, *Z. physik. Chem.*, 29 (1899), 242.
T.—Turner, *Z. physik. Chem.* 35 (1900), 385.
W.—Walden, *Z. physik. Chem.*, 70 (1909), 569.

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(1) Mizushima, This journal, 1 (1926), 47 & 83.

TABLE 1. Methyl alcohol.

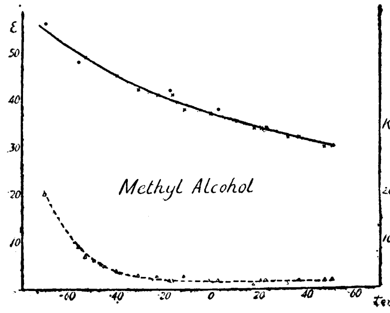
Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K\times 10^5$	ε (Other authors)
II	50	4.35	.58	4.35	30	2	
II	47	4.4	.58	4.4	30	2	
IV	46	5.7	.56	5.7	30	2	
II	36	4.7	.58	4.7	32	2	
III	31	5.4	.57	5.4	32	1	
IV	31	6.25	.59	6.25	32	1	
II	22	5.1	.58	5.1	34	2	
III	20	5.85	.56	5.85	34	2	
IV	17	6.8	.60	6.8	34	1	
—	13.4	—	—	—	—	—	35.3 (L.)
II	2	5.85	.56	5.85	38	2	
—	0	—	—	—	–	—	35.0 (A.S.)
I	− 1	4.65	.58	4.65	37	2	
I	−12	4.85	.53	4.85	38	3	
II	−17	6.4	.50	6.4	41	2	
II	−18	6.6	.50	6.6	42	2	
I	−23	5.25	.51	5.25	41	3	
I	−31	5.5	.48	5.5	42	3	
I	−40	5.9	.40	5.9	45	4	
—	−50	—	—	—	–	—	45.3 (A.S.)
I	−53	6.55	.28	6.55	49	7	
I	−56	6.55	.24	6.55	48	9	
II	−70	9.6	.08	9.25	56	20	

TABLE 2. Ethyl alcohol.

Vessel.	Temp.	$\Delta C'$	I/I_0	$\Delta C'$	ε	$K\times 10^5$	ε (Other authors)
I	54	2.35	.80	2.35	20.5	—	
II	53	2.9	.75	2.9	20	—	
—	50	—	—	—	—	—	20.5 (W.)

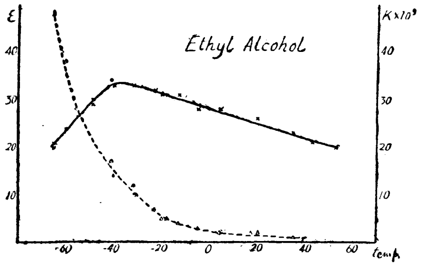
TABLE 2. *Continued.*

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K \times 10^5$	ε (Other authors)
II	43	3.1	.70	3.1	21	1	
I	35	2.7	.74	2.7	23	1	
II	20	3.85	.56	3.85	26	2	25.8 (A.S.)
I	17	3.05	.67	3.05	25	2	
—	14.7	—	—	—	—	—	26.8 (T.)
I	4	3.4	.58	3.4	28	2	
—	0	—	—	—	—	—	28.4 (A.S.)
I	− 5	3.5	.54	3.5	28	3	
I	−13	3.85	.46	3.85	31	4	
I	−18	4.0	.36	4.0	31	5	
I	−20	3.9	.35	3.9	31	5	
I	−23	4.05	.30	4.05	32	7	
I	−32	4.35	.18	4.3	33	12	
I	−40	4.4	.16	4.3	33	14	35.3 (A.S.)
I	−41	4.55	.14	4.45	34	17	
II	−49	5.25	.05	4.6	29	29	
I	−49	4.4	.07	3.9	30	29	
I	− 60	3.85	.05	3.15	24	38	
I	−65	3.6	.04	2.75	21	48	
II	−65	4.55	.03	3.15	20	48	



×.........Value of ε
△.........Value of K

Fig. 1.



×.........Value of ε
△.........Value of K

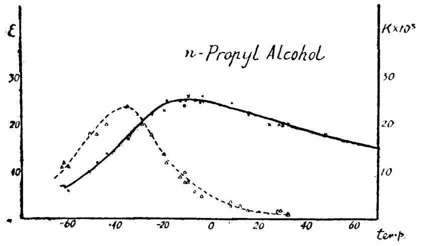
Fig. 2.

TABLE 3. Propyl alcohol.

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K \times 10^5$	ε (Other authors)
I	70	1.7	—	1.7	15	—	
IV	48	3.35	.76	3.35	18	<1	
IV	32	3.85	.64	3.85	20	1	
IV	29	3.85	.50	3.85	20	2	
I	29	2.3	.60	2.3	20	2	
I	28	2.35	.61	2.35	20	2	
I	24	2.35	.69	2.35	20	1	
—	20	—	—	—	—	—	22.2 (A.S.)
IV	15	4.35	.43	4.35	22	2	
—	14.3	—	—	—	—	—	22.4 (L.
IV	8	4.9	.33	4.9	24.5	3	
IV	8	4.9	.30	4.9	24.5	4	
—	0	—	—	—	—	—	24.8 (A.S.)
IV	− 4	5.3	.24	5.3	26	5	
III	− 7	4.3	.22	4.3	25	6	
IV	−10	5.35	.16	5.25	26	8	
III	−11	4.45	.18	4.4	25	8	
IV	−11	5.05	.13	4.9	24	10	
IV	−13	5.35	.14	5.2	25	9	
III	−19	4.7	.12	4.5	25	12	
I	−20	3.05	.16	2.95	23	14	
IV	−25	5.0	.07	4.5	22	18	
III	−29	4.15	.07	3.65	21	20	
I	−35	2.55	.09	2.1	17	24	
III	−44	3.0	.07	2.5	14	20	
III	−48	2.45	.08	2.05	12	18	
IV	−51	2.45	.07	1.95	10	18	
III	−60	1.1	.14	0.95	6	11	33.7 (A.S.)
	−62	0.9	.18	0.85	7	12	
IV	−63	1.5	.12	1.3	7	11	

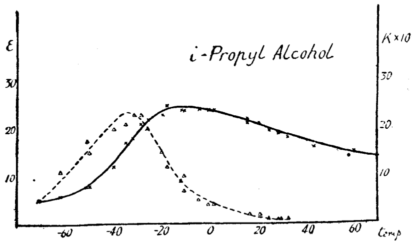
TABLE 4. Isopropyl alcohol.

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	I/I_0
III	70	2.2	—	2.2	14	<1
III	60	2.4	.83	2.4	15	<1
II	59	2.0	.86	2.0	14	<1
III	43	2.6	.78	2.6	16	<1
III	32	3.0	.68	3.0	18	1
II	31	2.65	.76	2.65	18.5	<1
III	29	3.1	.65	3.1	19	1
II	29	2.7	.67	2.7	19	1
III	28	3.15	.67	3.15	19	1
III	24	3.25	.59	3.25	19.5	1
IV	20	4.1	.48	4.1	21	2
III	15	3.65	.50	3.65	22	2
II	15	3.15	.47	3.15	21	2
III	1	4.05	.33	4.05	24	4
IV	− 1	4.9	.28	4.9	24	4
III	− 5	4.15	.24	4.15	24	5
III	−11	4.25	.20	4.25	24	7
II	−11	3.75	.17	3.65	24	10
IV	−12	5.05	.15	4.95	24	9
III	−18	4.65	.12	4.45	25	12
III	−20	4.4	.10	4.1	23	15
II	−26	3.75	.08	3.4	22	20
III	−29	4.25	.06	3.65	21	23
III	−32	3.75	.06	3.15	18	23
III	−35	3.65	.05	2.95	17	26
IV	−40	2.9	.06	2.25	12	20
III	−50	1.65	.10	1.35	8	15
II	−51	1.5	.10	1.2	8	17
III	−62	1.1	.13	0.9	6	11
II	−71	0.7	.30	0.7	5	5



×.........Value of ε
△.........Value of K

Fig. 3.



×.........Value of ε
△.........Value of K

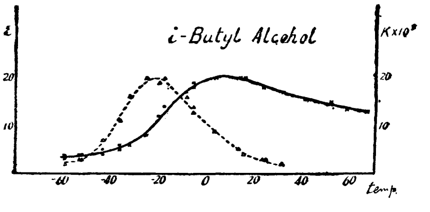
Fig. 4.

TABLE 5. Isobutyl alcohol.

Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K \times 10^5$	ε (Other authors)
IV	66	2.4	.90	2.4	13	<1	
III	58	2.15	.81	2.15	13.5	<1	
IV	51	2.8	.84	2.8	15	<1	
III	40	2.55	.70	2.55	15.5	<1	
IV	31	3.3	.58	3.3	17	2	
IV	24	3.5	.40	3.5	18	3	
III	23	3.05	.40	3.05	18	3	
III	22	3.0	.40	3.0	18	3	
—	18	—	—	—	—	—	18.9 (T.)
III	15	3.8	.27	3.8	20	4	18.7 (L.)
IV	14	3.3	.34	3.3	20	4	
III	14	3.35	.29	3.35	20	4	
III	13	3.45	.26	3.45	20	5	
IV	12	4.0	.25	4.0	20	4	
IV	3	4.1	.15	4.0	20	9	
—	0	—	—	—	—	—	21.8 (A.S.)
III	− 6	3.45	.11	3.2	19	14	
IV	− 6	3.85	.11	3.6	18	13	
IV	− 9	3.8	.08	3.4	17	16	
III	−18	2.85	.07	2.35	14	20	
III	−20	2.4	.07	1.95	12	19	
IV	−25	2.1	.06	1.45	8	20	
III	−32	1.25	.09	0.9	6	16	
III	−36	1.0	.13	0.85	6	11	
IV	−36	1.1	.12	0.9	5	11	
—	−40	—	—	—	—	—	27.0 (A.S.)
III	−43	0.75	.20	0.7	5	7	
IV	−43	0.8	.18	0.7	4	7	
III	−52	0.55	.34	0.55	4	3	
IV	−53	0.6	.37	0.6	4	3	
III	−59	0.5	.48	0.5	4	2	
IV	−59	0.55	.44	0.55	3	2	

TABLE 6. Amyl alcohol.

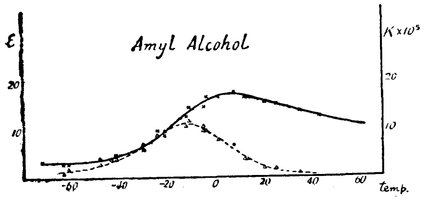
Vessel.	Temp.	ΔC	I/I_0	$\Delta C'$	ε	$K\times 10^5$	ε (Other authors)
IV	61	2.05	.88	2.05	11	<1	
III	60	1.7	.81	1.7	11	<1	
III	43	2.05	.72	2.05	13	<1	
IV	35	2.7	.63	2.7	14	1	
IV	25	2.95	.48	2.95	15.5	2	
II	20	2.3	.46	2.3	16	2	16.0 (A.S.)
—	13.8	—	—	—	—	—	16.6 (L.)
III	13	2.8	.30	2.8	17	4	
II	12	2.5	.34	2.5	17	4	
I	7.5	2.15	.30	2.15	18	7	
IV	1	3.25	.16	3.25	17	8	
—	0	—	—	—	—	—	17.4 (A.S.)
I	−4	2.05	.22	2.05	17	10	
IV	−5	3.2	.12	3.0	15	11	
III	−5	2.75	.15	2.6	15	10	
II	−11	2.35	.14	2.2	15	12	
III	−12	2.35	.13	2.15	13	11	
IV	−12	2.65	.11	2.45	13	11	
III	−21	1.7	.15	1.55	9	10	
IV	−21	1.85	.13	1.7	9	10	
I	−24	1.2	.23	1.2	10	9	
II	−30	0.95	.24	0.95	7	7	
IV	−30	1.1	.20	1.1	6	6	
I	−41	0.5	.42	0.5	5	4	
I	−43	0.4	.45	0.4	4	4	
II	−48	0.45	.44	0.45	4	3	
—	−50	—	—	—	—	—	23.0 (A.S.)
II	−61	0.3	.60	0.3	3	2	
I	−63	0.2	.74	0.2	3	1	



×.........Value of ε

△......... Value of K

Fig. 5.



×.........Value of ε

△.........Value of K

Fig. 6.

Table 7 contains the values of ε and K at every tenth degree of temperature obtained by graphical interpolation from the above results.

TABLE 7.

Temp.	Acetone	Glycerine		Methyl alcohol		Ethyl alcohol		Propyl alcohol		Isopropyl alcohol		Isobutyl alcohol		Amyl alcohol	
	ε	ε	$K \times 10^5$	ε	$K \times 10^5$	ε	$K \times 10^5$	ε	$K \times 10^5$	ε	$K \times 10^5$	ε	$K \times 10^5$	ε	$K \times 10^5$
70	—	35	<1	—	—	—	—	15	<1	14	<1	—	—	—	—
60	—	37	1	—	—	—	—	16	<1	15	<1	14	<1	11	<1
50	—	39	2	30	2	21	<1	17	<1	16	<1	15	<1	12	<1
40	—	40	4	31	2	22	1	19	<1	17	<1	16	<1	13	1
30	—	42	8	33	2	23	1	20	1	19	1	17	2	15	1
20	22	41	15	34	2	25	1	22	2	21	1	19	3	16	2
10	23	34	25	35	2	27	2	23	3	22	3	20	6	18	5
0	24	20	26	37	2	28	2	25	5	24	5	20	10	17	9
−10	25	12	12	39	2	30	4	25	8	25	8	17	15	15	11
−20	26	8	4	40	2	31	6	24	14	24	15	11	20	10	10
−30	27	5	2	42	3	33	10	20	22	19	23	7	17	7	7
−40	28	4	1	45	4	33	15	15	23	13	22	5	9	5	4
−50	29	4	<1	48	7	29	23	10	18	8	16	4	4	4	3
−60	30	4	<1	51	12	24	36	7	12	6	10	4	2	4	2
−70	31	4	<1	55	20	—	—	—	—	5	5	—	—	3	1

The behaviours of propyl, isopropyl, isobutyl, and amyl alcohols are, in general, quite similar to that of glycerine. At higher temperatures there is only little absorption and the values of ε obtained are found to be in good agreement with those measured at longer waves. As the temperature is gradually lowered, both ε and K increase, till each of them reaches its maximum respectively. The maximum of K lies at the point where the temperature coefficient of ε is nearly maximum. (See figures). At still lower temperatures, the values of K are decreasing and those of ε approaching to the square of the refractive indices for the visible light.

For ethyl alcohol, only the maximum of ε is obtained, and for methyl both of the maxima are not found. But it may be granted that at sufficiently low temperatures they will also behave as other alcohols.

As given above these alcohols show anomalous absorptions of the electric wave of the wave length of 9.5 metres as well as 6.1 metres, and these absorptions are incomparably greater than those expected from their electric conductivities. Anomalous changes of dielectric constants are observed at the same time. The point of maximum absorption lies always at the temperature at which the temperature coefficient of the anomalous change of ε is nearly maximum. The value of ε at this point is nearly equal to the mean of the dielectric constant at long wave lengths and the square of the refractive index for the visible light. From this fact it can evidently be expected that if the change of ε by the wave length be studied at constant temperature, the point of the maximum change of ε (i. e. the point where the dispersion is most anomalous) will be accompanied by a very strong absorption of the wave. Experiments are now continued with waves of different wave lengths in order to obtain the data necessary for the study of the above relation and its analogy to that between the anomalous dispersion and absorption of the visible light.

The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

October 31, 1925,

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MELTING CURVES OF THE SYSTEMS HYDROGEN CHLORIDE–ETHYL ETHER AND HYDROGEN CHLORIDE–ACETONE.

By **Masao HIRAI.**

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Melting curves of the system hydrogen chloride- ethyl ether was already studied by O. Maass and D. McIntosh⁽¹⁾ in 1913. These authors obtained a result that there exists three compounds $(HCl)(C_4H_{10}O)$, $(HCl)_2(C_4H_{10}O)$, and $(HCl)_5(C_4H_{10}O)$. I have recently studied this system again, together the system hydrogen chloride-acetone, and are described in the following.

The System Hydrogen Chloride–Ethyl Ether. A small quantity of pure dehydrated ether is introduced into a glass bulb of about 1.5 c.c. capacity and weighed. The bulb is then connected to a reservoir of pure dry hydrogen chloride gas, and cooled by liquid air. The hydrogen chloride condenses into the bulb, the quantity of which can roughly be estimated by the pressure change and the volume of the gas reservoir. The bulb is, then, hermetically sealed and is put in a bath of low temperature. The bath is made of a non-silvered Dewar vessel containing petroleum ether, which is cooled by

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(1) Maass and McIntosh, *J. Am. Chem. Soc.*, 35 (1913), 537.

dropping liquid air. The melting of the mixture in the bulb can be seen from the outside of the vessel, and the temperature was measured by three series copper-constantan thermocouples which is kept by the side of the bulb.

The composition of the mixture was determined in the following manner. The bulb is taken out after the melting point was observed, and brought into a thick walled glass bottle which containing some water in it. The bottle is, then, shaken vigorously so that the bulb is broken and the hydrogen chloride gas is absorbed by the water. The hydrochloric acid solution thus produced is then titrated with alkali solution.

The results of the experiments are as follows.

Mol % of HCl.	Melt. pt.	Mol % of HCl.	Melt. pt.
0 (pure ether)	−117.7°	63.71	− 87.4°
10.84	−118.8	68.30	− 89.0
13.07	−119.3	72.61	− 93.5
20.32	−124.2	78.94	−100.4
22.67	−127.8	81.24	−104.0
31.96	−126.5	88.80	−113.5
36.34	−115.4	89.45	−115.5
40.45	−110.9	93.92	−123.6
47.87	−100.4	94.24	−123.7
49.03	−100.9	95.35	−120.8
52.82	−107.3	96.13	−120.5
55.16	− 94.5	100.00 (pure HCl)	−112.5
61.76	− 89.3		

Graphically it becomes as Fig. 1. From this figure it is evident that there exists only one compound $(HCl)_2 (C_4H_{10}O)$ which melts at −87.3°.

The System Hydrogen Chloride–Acetone. The experimental procedure is quite same as the system mentioned above. The results are as follows.

Mol % of HCl.	Melt. pt.	Mol % of HCl.	Melt. pt.
0 (pure acetone)	− 94.5°	45.12	−81.7
14.43	−107.0	52.91	−80.0
20.50	−111.4	55.56	−82.7
27.29	−114.6	57.26	−86.6
31.78	−104.2	60.39	−92.8
42.99	− 85.7		

Fig. 1.

Fig. 2.

Graphically it becomes as Fig. 2. In this case, there is one compound (HCl) (C_3H_6O), whose melting point is −79.0°. In the part where the amount of hydrogen chloride exceeds 60 percent, the mixture became glassy mass by cooling and could not determine the melting point.

The author's thanks are due to Prof. J. Sameshima for his kind guidance.

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SYNTHESIS OF METHOXY-HYDROXY-N-METHYL-3·4-DIHYDROISOQUINOLINIUM SALTS.

By Shirō AKABORI.

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(Continued from Page 102)

6-Methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium Salts (VIII). 1 gram of 6-methoxy-7-benzyloxy-2-methyl-3·4-dihydroisoquinolinium chloride and 3 c.c. of concentrated hydrochloric acid were slightly warmed on a water-bath. The solution became gradually opaque and finally deposited oily drops of benzyl chloride. When the solution was separated from benzyl chloride and evaporated in a vacuum over potassium hydroxide, 6-methoxy-7-hydroxy-2-methyl-3.4-dihydroisoquinolinium chloride (VIII) remained as a crystalline mass. This was recrystallized from a mixture of methyl alcohol and acetone, from which it was deposited in the form of yellow glistening plates. It melts and decomposes at 187°, after sintering at 155°. Sometimes it crystallized in needles which frothed at 150–153°, after sintering at 140°.

0.1254 gr. subst. became 0.1161 gr. after being dried in a vacuum at 80°, and gave 0.0715 gr. AgCl. 8.74 mg. subst. gave 0.425 c.c. nitrogen (12°, 755.4 mm.) (Found: $H_2O=7.42$, $Cl=14.11$, $N=5.83$. $C_{11}H_{14}O_2NCl.H_2O$ requires $H_2O=7.34$, $Cl=14.44$, $N=5.70$ %).

The iodide is readily obtained by the action of potassium iodide on the aqueous solution of the chloride; decomp. p. 213° (corr. 218°).⁽¹⁾

0.1127 gr. subst. gave 0.0820 gr. AgI. 5.85 mg. subst. gave 4.28 mg. AgI (methoxyl). (Found: $I=39.33$, $CH_3O-=9.67$. $(CH_3O)-C_{10}H_{11}ONI$ requires $I=39.78$, $CH_3O-=9.72$ %).

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(1) Compare F. L. Pyman, *J. Chem. Soc.*, 97 (1910), 278.

The perchlorate crystallizes in white needles, which melt at 196–197°.

6-Methoxy-7-hydroxy-2-methyl-3·4-dihydroisoquinolinium salts dissolve in dilute alkali to deep yellow solutions, which on a further addition of a concentrated solution of caustic alkali become colourless, and, on dilution with water, regain their colour. The picrate of this base shows peculiar phenomena; the aqueous solution of the chloride, when mixed with aqueous picric acid first deposits yellow needles, which on being gently heated, or on standing for several hours, are converted into orange-red prisms, and these when left standing for many days, or on being boiled with water,—but in not sufficient quantity to dissolve them all—, once more turn to yellow granular crystals. The orange-red modification contains one molecule of the water of the crystallization; m. p. 92°.

0.1522 gr. subst. became 0.1465 gr. after being dried in a vacuum at 56°. (Found: $H_2O=4.19$. $C_{17}H_{16}O_9N_4 \cdot H_2O$ requires $H_2O=4.11$ %).

The yellow granular modification is the most stable and anhydrous; m. p. 159–160°.

0.0787 gr. subst, gave 0.1396 gr. CO_2 and 0.0296 gr. H_2O. (Found: C=48.38, H=4.21. $C_{17}H_{16}O_9N_4$ requires C=48.55, H=3.84 %).

6·7-Dihydroxy-2-methyl-3.4-dihydroisoquinolinium Chloride (IX). 2 grams of hydrostinine and 5 grams of phosphorus pentachloride were heated in a sealed tube at 145–150° for five hours. After being cooled to room temperature, the tube was opened and 10 c.c. of alcohol was poured in, when a copious evolution of gas took place and 6·7-dihydroxy-2-methyl-3·4-dihydroisoquinolinium chloride separated as a yellow crystalline powder. This was purified by recrystallization from glacial acetic acid, from which it was deposited in anhydrous prisms, decomp. p. 268° (corr. 276°). All its properties are in agreement with the description given by Pyman.⁽¹⁾

0.1467 gr. subst. gave 0.0993 gr. AgCl. (Found: Cl=16.75. $C_{10}H_{12}O_2NCl$ requires Cl=16.60 %).

On addition of sodium carbonate to a concentrated solution of chloride IX, the phenolbetaine of 6·7-dihydroxy-2-methyl-3·4-dihydroisoquinolinium hydroxide separates in deep yellow glistening leaflets. The same compound is also obtained from compound VIII in the same way as was done by Pyman from 6·7-dimethoxy-2-methyl-3·4-dihydroisoquinolinium chloride.

Action of Methyl Iodide on the Phenolbetaine of 6·7-Dihydroxy-2-methyl-3·4-dihydroisoquinolinium-hydroxide. 1 gram of finely powdered anhydrous phenolbetaine and 3 grams of methyl iodide were heated together in a sealed tube for 3 hours at 100°. The product was dissolved in water, treated with a concentrated solution of potassium iodide, when 6-

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(1) Pyman, loc. cit., p. 275.

methoxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium iodide separated as yellow crystals (0.6 gram). It was easily purified by recrystallization from alcohol; decomp. p. 213° (corr. 218°).

8.79 mg. subst. gave 6.45 mg. AgI. 6.92 mg. subst. gave 4.95 mg. AgI (methoxyl). (Found: I=39.66, CH_3O- =9.45. $(CH_3O)-C_{10}H_{11}ONI$ requires I=39.78, CH_3O-=9.72 %).

The chloride was prepared by digesting the alcoholic solution of the iodide with freshly precipitated silver chloride; decomp. p. 187°. When the picrate (m. p. 159–160°) was mixed with the picrate of synthesized 6-methoxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium base, no depression of the melting point occurred.

6-Benzyloxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium iodide (XI). 1.6 grams of phenolbetaine and 3 grams of benzyl iodide were heated together for half an hour on a bath of boiling water. The excess of benzyl iodide was removed by trituration with absolute ether. After fractional crystallization from hot water, two compounds were isolated from the product; the one is readily soluble in hot water, while the other is only slightly soluble. The former is soluble in dilute alkali to a deep yellow solution, a behaviour exactly similar to that of 6-methoxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium salt. The result of analysis agreed with 6-benzyloxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium iodide; m. p. 189–190°. Yield 1.5 grams.

16.15 mg. subst. gave 9.53 mg. AgI. (Found: I=31.90. $C_{17}H_{18}O_2NI$ requires I=32.11 %).

The latter is insoluble in alkali, and is nothing but 6•7-dibenzyloxy-2-methyl-3•4-dihydroisoquinolinium iodide; m.p. 194–195°. Yield 0.5 gram.

13.85 mg. subst. gave 6.68 mg. AgI. (Found: I=26.07. $C_{24}H_{24}O_2NI$ requires I=26.18 %).

6-Benzyloxy-7-(6-benzyloxy-7-hydroxy-2-methyl-3•4-dihydroisoquinoliniumoxy)-2-methyl-3•4-dihydroisoquinolinium Iodie (XII). When a concentrated solution of compound XI was treated with potassium carbonate, orange coloured oily drops were deposited, which on standing for many days, were converted into orange prisms. After recrystallization from alcohol it melted at 196–198°. This still contains iodine, and is assumed to have the constitution of XII.

11.26 mg. subst. gave 4,02 mg. AgI. (Found: I=19.30. $C_{17}H_{18}O_2N$-O-$C_{17}H_{17}ONI$ requires I=19.16 %).

6-Benzyloxy-7-hydroxy-2-methyl-3•4-dihydroisoquinolinium Salts (XIII.) The mixture of 1 gram of the above mentioned compound (XII) and 0.5 gram of methyl iodide was left at room temperature for one day. At the end of the reaction the orange colour changed to a pale yellow. The product was dissolved in water, treated with a concentrated solution of sodium hydroxide, and extracted with ether. The ethereal solution was shaken with water containing a little hydrochloric acid, whereby the aqueous layer exhibited a green fluorescence. On addition of picric acid to this aqueous solution, precipitation of yellow crystalline picrate took place. After repeated crystallization from alcohol this picrate formed yellow leaflets, which melted at 176–177°. On mixing with 6-methoxy-7-benzyloxy-2-methyl-3·4-dihydroisoquinolinium picrate, it melted at 150–160°.

6.11 mg. subst. gave 0.554 c. c. nitrogen (22°, 761 mm.) (Found: N=10.74. $C_{24}H_{22}O_9N_4$ requires N=10.98 %).

The perchlorate crystallizes in beautiful needles exhibiting a green fluorescence. This is almost insoluble in water but moderately soluble in alcohol; m. p. 222–225°.

ClO_4 in perchlorates was estimated as nitron perchlorate, according to the method of Fichter and Schmidt.(1) In filtering and weighing the precipitate, Pregl's microfiltering tube was employed with good results. The accuracy of this method was confirmed in the case of several known substances.

12.78 mg. subst. gave 14.01 mg. $C_{20}H_{16}O_4 \cdot HClO_4$. (Found: ClO_4=26.42. $C_{18}H_{20}O_2NClO_4$ requires ClO_4=26.06%);

6-Hydroxy-7-methoxy-2-methyl-3·4-dihydroisoquinolinium Salt (XIV). 15 milligrams of 6-benzyloxy-7-methoxy-2-methyl-3·4-dihydroisoquinolinium perchlorate were treated with 2 c. c. of concentrated hydrochloric acid. After the crystals had all dissolved, the solution was evaporated in a vacuum, and the residue was crystallized from alcohol, from which it separated in the form of slightly brownish coloured, spear-head-like crystals, m. p. 178–179.5°. Yield 10 milligrams. This is easily soluble in alcohol or water to light yellow greenish fluorescent solutions. With ferric chloride the solutions give no colouration.

7.12 mg. subst. gave 10.19 mg. $C_{20}H_{16}N_4 \cdot HClO_4$. (Eound: ClO_4=34.50. $C_{11}H_{14}O_2NClO_4$ requires ClO_4 =34.11%).

The writer wishes to express his sincere thanks to Professor Dr. R. Majima and Dr. S. Kobayashi for their kind guidance and continued encouragement during the course of this work.

(The end)

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(1) *Z. anorg. Chem.*, 98 (1916), 142.

THE CONDENSATION OF RESORCINOL WITH ETHYLENE DICYANIDE.

By Junkichi MURAI.

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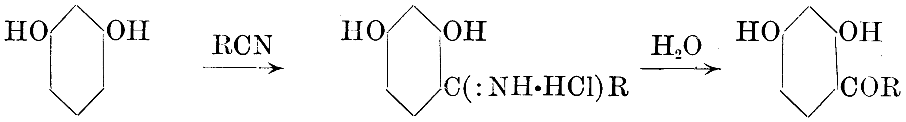
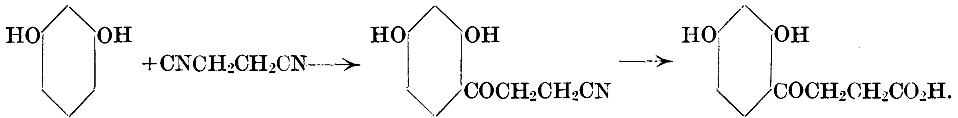
Since Hoesch(1) first discovered that nitriles reacted with certain phenols, in the presence of anhydrous zinc chloride and dry hydrogen chloride, to give aromatic hydroxy-ketones according to the following scheme :



this reaction has been applied extensively in the preparation of carbonyl compounds. Sonn(2) applied this method to a dicyanide and found that o-cyanoacetyl phloroglucinol, $CNCH_2CO \cdot C_6H_2(OH)_3$, and 2:4:6:2′:4′:6′-hexahydroxydibenzoylmethane, $C_6H_2(OH)_3COCH_2COC_6H_2(OH)_3$, were obtained by the condensation of malonitrile with phloroglucinol.

With the view of synthesising phenolic γ-diketones, the author attempted to condense resorcinol with ethylene dicyanide by Hoesch's method. However, the action of ethylene dicyanide on resorcinol resulted in the production of a compound, which, from its composition and method of formation, was regarded as β-2:4-dihydroxybenzoylpropionic acid (I) :



(I)

The constitution of this acid was confirmed beyond doubt by the preparation of its salt, and by the formation of the dibenzoyl derivative and of the oxime of the dimethyl derivative.

Experimental.

Synthesis of β-2:4-Dihydroxybenzoylpropionic Acid, $C_6H_3(OH)_2COCH_2CH_2CO_2H$. (a) Twenty two grams of resorcinol (2 mols) and 8 grams of ethylene dicyanide (1 mol) were dissolved in absolute ether (100 c. c.) and, after the addition of 8 grams of freshly fused and powdered zinc chloride, a gentle stream of dry hydrogen chloride was passed into the liquid for four hours, the mixture being kept warm during this operation, when a red syrup

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(1) *Ber.*, 48 (1915), 1122.

(2) *Ber.*, 50 (1917), 1292.

separated. After allowing to remain overnight and decanting the ether, the syrup was dissolved in 150 grams of ice-cold water, concentrated to about 100 c. c. on the water-bath and then cooled. The dark brown substance thus separated was crystallised once from water with the addition of animal charcoal, when it separated in grey crystals melting at 197–199.° The yield was 5.7 grams. As it is difficult to obtain these crystals so that they are free from any mineral matter by further recrystallisation, the acid was converted into its sodium salt, and, after recrystallising from water, the salt was acidified with hydrochloric acid, in order to regenerate the free acid, and again recrystallised several times from water. It was colourless crystals melting at 199–200°:

4.297 mg. subst. gave 9.020 mg. CO_2 and 1.966 mg. H_2O. (Found: $C=57.25$; $H=5.12$. $C_{10}H_{10}O_5$ requires $C=57.12$; $H=4.80\%$).

(b) Since the interaction between resorcinol (2 mols) and ethylene dicyanide (1 mol) resulted in the formation of β-2:4-dihydroxybenzoylpropionic acid, the condensation was again carried out under the same conditions as in (a), except that 11 grams of resorcinol (1 mol) were used. The yield of β-2 : 4-dihydroxybenzoylpropionic acid was 5.7 grams after once crystallising from water.

The Sodium Salt. For the preparation of this salt, 3 grams of the crude β-2:4-dihydroxybenzoylpropionic acid were shaken with a concentrated solution of sodium carbonate until the evolution of carbon dioxide had ceased. The salt thus obtained was collected and recrystallised from small quantity of water, when it separated in colourless crystals (yield 3.9 grams). The air-dried salt lost 18.53% in weight when heated at 130° under reduced pressure. The anhydrous salt gave, on analysis, the following results:

5.154 mg. subst. gave 1.282 mg. Na_2SO_4 and 4.347 mg. subst. gave 1.102 mg. Na_2SO_4. (Found: $Na=8.05$ and 8.21. $C_{10}H_9O_5Na{\cdot}3H_2O$ requires $H_2O=18.89$; $Na=8.04\%$.)

The Benzoyl Derivative One gram of β-2:4-dihydroxybenzoylpropionic acid was dissolved in 5.5 c.c. of a 10% solution of sodium hydroxide and shaken with 1.1 c.c. of benzoyl chloride for two hours. After acidifying with dilute hydrochloric acid, the precipitate was collected, washed with water and dried (yield 1.3 grams). It crystallised from dilute methyl alcohol in colourless crystals, m. p. 146–147°:

4.698 mg. subst. gave 11.840 mg. CO_2 and 1.931 mg. H_2O. (Found: $C=68.73$; $H=4.59$. $C_{24}H_{18}O_7$ requires $C=68.88$; $H=4.34\%$).

β-2:4-Dimethoxybenzoylpropionic Acid, $C_6H_3(OCH_3)_2COCH_2CH_2CO_2H$. β-2:4-Dihydroxybenzoylpropionic acid (5 grams) was dissolved in 25 c.c. of a 10% sodium hydroxide and shaken with 4.5 c.c. of methyl sulphate for two hours, when a small quantity of oil deposited, which was extracted with ether. The aqueous residue (A) and the ethereal extract (B) were treated in the following way.

The aqueous residue (A) was acidified with dilute hydrochloric acid and the precipitate was collected, washed with water and dried. After recrystallising several times from methyl alcohol with the addition of animal charcoal, it separated in colourless crystals and melted at 124–125.° The yield was 4.5 grams after one crystallisation.

The ethereal extract (B) was washed with water until free from alkali. After the evaporation of the ether, the residual oil was hydrolysed by warming it with a dilute solution of sodium hydroxide and the alkaline solution was acidified with hydrochloric acid. The precipitate was collected, washed with water, dried, and recrystallised from alcohol, when it melted at 124–125° and produced no depression of the melting point by admixture with β-2:4 dimethoxybenzoylpropionic acid:

4.645 mg. subst. gave 10.262 mg. CO_2 and 2.473 mg. H_2O. (Found: C=60.25; H=5.96. $C_{12}H_{14}O_5$ requires C=60.48; H=5.93 %).

The Oxime. A mixture of β-2:4-dimethoxybenzoylpropionic acid (0.2 gram), hydroxylamine hydrochloride (0.06 gram) and sodium acetate (0.12 gram) was dissolved in dilute alcohol and boiled for two hours under a reflux condenser. After the removal of the alcohol, the oxime separated, which crystallised from dilute methyl alcohol as colourless crystals melting at 155–156.° The quantity of the crude oxime amounted to 0.2 gram:

6.516 mg. subst. gave 0.307 c. c. nitrogen at 13° and 755.3 mm. (Found: N=5.59. $C_{12}H_{15}O_5N$ requires N=5.53%).

In conclusion, the author wishes to express his hearty thanks to Dr. Hiroshi Nomura, in whose laboratory this investigation was carried out.

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ON THE MECHANISM OF THE SUBSTITUTION REACTION OF TRANS-DICHLORO-DIETHYLENEDIAMINE COBALTIC CHLORIDE IN ITS AQUEOUS SOLUTION.

By Kichimatsu MATSUNO.

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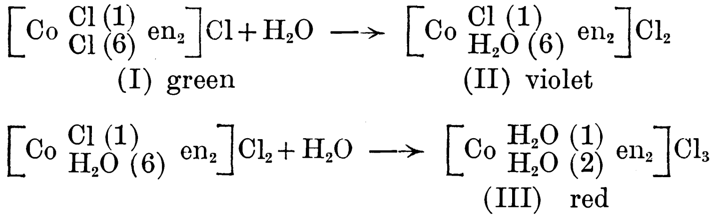
Introduction. In the previous paper⁽¹⁾ it has been shown that the chemical changes in aqueous solutions of some cobaltammines could be followed by utilising the valency effect on the coagulation of arsenious sulphide sol. The present investigation was undertaken by the same method, to study the kinetics of the change of trans-dichloro-diethylenediamine cobaltic chloride, $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}$, in its aqueous solution. It is well known that the aqueous solution of this salt changes its colour gradually from green to violet and finally to red. This colour change is generally considered to be due to the following reactions which take place in the solution,⁽²⁾



$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}+\mathrm{H_2O}\longrightarrow\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{H_2O}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}_2$$

$$\text{(I) green}\qquad\qquad\text{(II) violet}$$

$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{H_2O}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}_2+\mathrm{H_2O}\longrightarrow\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\,(1)\\ \mathrm{H_2O}\,(2)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}_3$$

$$\text{(III) red}$$

As seen in the above formulae, the substitution of chlorine atoms by water molecules in the complex radicals causes not only the colour change but also the increase of the valency of the complex ions of the salts thus produced. The substitution reactions above mentioned may, therefore, be easily followed by observing the colour change as well as the electrolytic conductivity of the solution,⁽³⁾ and also by means of the coagulation of arsenious sulphide sol.

The last method consists in measuring from time to time the limiting concentrations of the solution which just failed to produce any perceptible

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(1) K. Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, Vol. 41, Art. 11 (1921).

(2) Werner, *Ann. Chem.*, 386 (1912), 54.
Y. Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, Vol, 37, Art. 2 (1915), 25.
K. Matsuno, ibid., Vol. 41, Art. 10 (1921), 19.

(3) Compare Werner and Herty, *Z. physik. Chem.*, 38 (1901), 341; Lamb and Marden, *J. Am. Chem. Soc.*, 33 (1911), 1787.

coagulation of arsenious sulphide sol within five minutes. The present experiments were carried on with the same sample of arsenious sulphide sol as in the former experiment, so that the empirical formula previously deduced could be used in the following calculations without any transformation. It will be seen that the limiting concentrations thus measured are related to the actual concentrations of the complex salts in the solution and from the sequel the velocity constants of the substitution reactions can be calculated.

Theoretical. As regards to the concentrations of each salt in the solution of $\left[\mathrm{Co}\,\substack{\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)}\,\mathrm{en}_2\right]\mathrm{Cl}$, which were very difficult to estimate, they could be connected with the limiting concentrations by the following consideration.

Let the concentrations of (I), (II) and (III) at the time t be C_A, C_M and C_B respectively, the velocities of decreasing of the first salt and increasing of the last salt will be :

$$\frac{-dC_A}{dt}=k_1C_A \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$\frac{dC_B}{dt}=k_2C_M \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

The velocity of the formation of the intermediate salt is :

$$\frac{dC_M}{dt}=-\frac{dC_A}{dt}-\frac{dC_B}{dt} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

By integration, C_A, C_M and C_B can be obtained as follows :

$$\left.\begin{aligned} C_A&=C_{0A}e^{-k_1t}\\ C_M&=C_{0A}\frac{k_1}{k_2-k_1}\left(e^{-k_1t}-e^{-k_2t}\right)\\ C_B&=C_{0A}\frac{k_1\,k_2}{k_2-k_1}\left(\frac{1}{k_2}e^{-k_2t}-\frac{1}{k_1}e^{-k_1t}\right)\end{aligned}\right\}\cdots\cdots\cdots (4)$$

where C_{0A} denotes the initial concentration and is equal to the sum of C_A, C_M and C_B.

In the substitution reaction in question, the limiting concentration is denoted by S which was assumed to be related to each other as below :

$$S_1\times\frac{C_A}{C_{0A}}+S_2\times\frac{C_M}{C_{0A}}+S_3\times\frac{C_B}{C_{0A}}=S \quad \cdots\cdots\cdots\cdots (5)$$

S_1, S_2 and S_3 represent the values corresponding to the monovalent, divalent and trivalent cations respectively.

This assumption implies the fact that the coagulation of the sol by the electrolytes is purely an adsorption phenomenon.

In the previous paper (loc. cit.), it was shown that the relation between the valency of the complex radicals of the cobaltammines and their coagulating power on arsenious sulphide sol may be expressed by the following equation :

$$S_n = S_1 \times \frac{1}{N^4} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

where S_n is the limiting concentration (eq. mol) of an N-valent complex ion. Combining (5) with (6), we obtain

$$C_A + \frac{1}{2^4} C_M + \frac{1}{3^4} C_B = \frac{C_{0A}}{S_1} S \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (7)$$

Eliminating the term of the concentrations by the substitution of (4) in (7), we get the following equation :

$$\frac{S-S_3}{S} = 1 - \frac{1}{k_1-k_2}\left(\frac{k_1}{2^4} - \frac{k_2}{3^4}\right)e^{-k_1t} + \left(\frac{1}{2^4} - \frac{1}{3^4}\right)\frac{k_1}{k_1-k_2}e^{-k_2t} \cdots\cdots (8)$$

Since S_1 and S_3 were known in the previous experiment, the equation (8) may be solved, if we could determine k_1 and k_2.

In order to determine these velocity constants, the initial and the last state of the reaction were considered. In the beginning of the reaction, we can assume $C_A + C_M = C_{0A}$ neglecting C_B which will be very small compared with C_A and C_M.

The velocity of decaying of the starting substance is

$$-\frac{dC_A}{dt} = k_1 C_A.$$

Now combining the following two equations

$$C_A + C_M = C_{0A}$$

$$S_1 C_A + S_2 C_M = C_{0A} S$$

we get

$$(S_1 - S_2) C_A = C_{0A}(S - S_2)$$

or

$$C_A = \frac{C_{0A}}{S_1 - S_2}(S - S_2).$$

Then, by the integration of the above mentioned velocity equation, we get

$$C_A = C_{0A} e^{-k_1 t}$$

and by the substitution,

$$\frac{S - S_2}{S_1 - S_2} = e^{-k_1 t}.$$

Using the common logarithm,

$$k_1=\frac{2.303}{t}\log\frac{S-S_2}{S_1-S_2}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\ (9)$$

By the equation (9), k_1 was now calculated as below, taking $S_1=56$ and $S_2=20$.

TABLE 1.

Time (min.)	$S\times 60000$	k_1	mean
22.5	48	0.0111	0.011
56.0	40	0.0105	
92.0	30	0.0139	
120.5	20	0.172	

In the next calculation, the mean value of the first two of the third column in Table 1, namely $k_1=0.011$, was taken.

In the last stage of the substitution reactions, it is expected that there remains so small quantity of the trans-dichloro-diethylenediamine cobaltic chloride that it can be neglected as compared with those of the intermediate and the final salts. A quite similar method of computation can be applied to determine k_2, which is formulated as follows :

$$C_M+C_B=C_{0A}$$

$$S_2C_M+S_3C_B=C_{0A}S$$

$$(S_3-S_2)C_B=C_{0A}(S-S_2)$$

$$C_B=\frac{C_{0A}}{S_3-S_2}(S-S_2)$$

$$\frac{dC_B}{dt}=k_2(C_M-C_B).$$

By integration

$$-\ln\frac{C_{0A}}{S_2-S_3}(S-S_3)=k_2t+\text{const.}$$

$$\ln\frac{S'-S}{S''-S_3}=k_2(t''-t')$$

or

$$k_2=\frac{2.303}{t''-t'}\log\frac{S'-S_3}{S''-S_3}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(10)$$

Table 2 shows the values of k_2, the mean of which, $k_2=0.0031$, was taken in the further calculation.

TABLE 2.

Time (min.)	$(S-S_3)\times 60000$	$t''-t'$	k_2
120.5	20	507	0.00317
154	16	473	0.00293
193	15	434	0.00304
259	13	368	0.00319
382	9	245	0.00330
507	6	120	0.00337
627	4	—	—

Now that $k_1=0.011$ and $k_2=0.0031$ had been determined, the equation (8) has been solved as below:

$$\frac{S-S_3}{S_1}=0.918\,e^{-0.011t}+0.0698\,e^{-0.0031t}\quad\cdots\cdots(11)$$

Experimental. The method of determining the limiting concentration was entirely the same as in the previous case (loc. cit.) One c.c. of the sol was placed in each of ten carefully cleaned test-tubes of Jena glass which were kept in a thermostat regulated to be 25°C. A certain amount of the salt solution, kept in the same temperature, was taken out, from time to time and each set of the solutions of different dilutions were quickly prepared. Two c.c. of them were added to each of one c.c. of the sol. During addition, the tube were vigorously shaken to ensure thorough mixing. In this way two such concentrations were obtained that the lower did not show any perceptible coagulation whereas the higher did. This concentration was then more carefully examined if necessary and thus the limiting concentration was determined.

(1) (6) Dichloro-diethlenediamine cobaltic chloride, $\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\,\mathrm{en}_2\right]\mathrm{Cl}$, which was used in this study was freshly prepared.(1) From the nature of this kind of experiments, an accuracy of high grade could not be expected. In Table 3, S (calc.) denotes the limiting concentration calculated by the equation (11), which could be compared with S (obs.). The theoretical values were fairly well concordant with the experimental. (See Table 3 and Fig. 1).

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(1) Joergensen, *J. prakt. Chem.*, (2) 39 (1889), 16.

TABLE 3.

Time (min.)	S (obs.)	S (calc.)
0	$56\times\frac{1}{60000}$	—
22.5	48 "	$51.8\times\frac{1}{60000}$
56	40 "	39.1 "
92	30 "	29.6 "
120.5	24 "	24.3 "
154	20 "	19.9 "
193	19 "	16.3 "
259	17 "	12.7 "
382	13 "	10.0 "
507	10 "	9.0 "
627	8 "	8.6 "

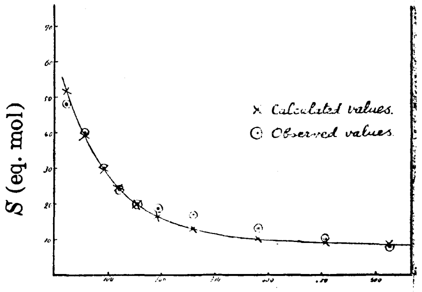


Fig. 1. Time (min.)

As regard the intermediate compound, $\left[\mathrm{Co}\begin{smallmatrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{smallmatrix}\ \mathrm{en}_2\right]\mathrm{Cl}_2$, its concentration will become maximum, when

$$\frac{dC_M}{dt}=0$$

or

$$C_{0A}\times\frac{k_1}{k_2-k_1}\left(k_2\,e^{-k_2t}-k_1\,e^{-k_1t}\right)=0$$

Replacing $k_1=0.011$, $k_2=0.0031$ and equating $k_2e^{-k_2t}-k_1e^{-k_1t}=0$, we could easily find the time when the concentration of $\left[\mathrm{Co}\begin{smallmatrix}\mathrm{Cl}\ (1)\\ \mathrm{H_2O}\ (6)\end{smallmatrix}\ \mathrm{en}_2\right]\mathrm{Cl}_2$ was maximum. Namely,

$$t=\frac{2.303}{0.0079}(\log 0.011-\log 0.0031)=160.^{\text{min.}}$$

The second differential of C_M, d^2C_M/dt^2, is equal to

$$C_{0A}\frac{k_1}{k_2-k_1}\left(k_1^2\,e^{-k_1t}-k_2^2\,e^{-k_2t}\right).$$

At the point where $d^2C_M/dt^2=0$, we find an inflexion point, the time of which could be calculated as below:

$$t=\frac{2.303\times 2\,(\log k_1-\log k_2)}{k_1-k_2}=320.^{\text{min.}}$$

Similarly the inflexion point on the velocity curve of the final product of the substitution reactions could be computed thus:

$$\frac{d^2C_B}{dt^2}=\frac{C_{0A}k_1k_2^2}{k_2-k_1}e^{-k_2t}-\frac{C_{0A}k_1^2k_2}{k_2-k_1}e^{-k_1t}=0$$

or

$$k_2\,e^{-k_2t}=k_1\,e^{-k_1t}$$

Substituting $k_1=0.011$ and $k_2=0.0031$, we get $t=160^{\text{min.}}$

The inflexion point of C_B curve coincide with the maximum point of C_M curve. (See Fig. 2).

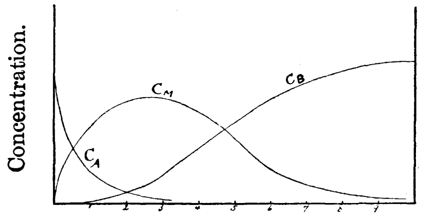
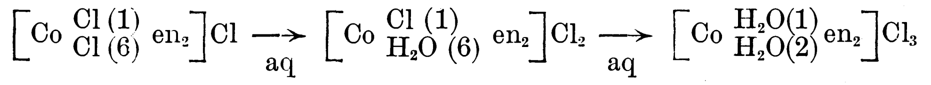


Fig. 2. Time (hour)

Summary.

1. By means of the coagulation of arsenious sulphide sol, the mechanism of the substitution reactions,



$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{Cl}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}\xrightarrow[\mathrm{aq}]{}\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\,(1)\\ \mathrm{H_2O}\,(6)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}_2\xrightarrow[\mathrm{aq}]{}\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}(1)\\ \mathrm{H_2O}(2)\end{matrix}\mathrm{en}_2\right]\mathrm{Cl}_3$$

has been studied, and it has been proved that this change is a monomolecular successive reaction.

2. The velocity constants of the first and second reaction of the substitution above mentioned has been calculated as $k_1=0.011$ and $k_2=0.0031$.

3. The time when the intermediate compound would be in its maximum concentration could be computed.

The author is indebted to Prof. Yuji Shibata for his kind advice and to Mr. Haruto Tsukamoto, professor of chemistry in the Hamamatsu Technical High School, for his kind assistance.

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A STUDY OF THE RECIPROCAL SALT PAIR: $[K_2, (NH_4)_2] - [SO_4, CrO_4]$ AT 25°C.

By **Tadashi ISHIKAWA.**

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In a systematic study of a reciprocal salt pair, it is necessary to know the solubilities of the four single salts and the equilibria of the systems of two salts with a common ion and water, previous to the study of the equilibrium of the system in question. In the present case of $[K_2, (NH_4)_2]-[SO_4, CrO_4]$, the necessary data for those equilibria are found in literature.(1) As to the systems of two salts with a common ion, the following facts are to be remarked, all being observed at 25°. Potassium sulphate and potassium chromate, and ammonium sulphate and potassium sulphate form a complete series of solid solutions under the liquid solutions respectively, with no gap. Ammonium chromate and ammonium sulphate, and ammonium chromate and potassium chromate form each two series of solid solutions with a gap. The gaps are respectively 2.90 – 21.50 and 16.75 – 55.50 in molar percentage of ammonium chromate.

Materials. The four salts were "extra pure" preparations of E. Merck and have been tested for their purity according to Merck's "*Prüfung der chemischen Reagenzien auf Reinheit.*" Ordinary distilled water was used.

Methods of Analysis. The chromate was estimated by the ordinary method of iodometry. The ammonium was determined by distillation of the sample with caustic soda into a known volume of a standard sulphuric acid and titrating back the excess of the acid with a standard alkali solution, using methyl orange as indicator. The sulphate was determined as barium sulphate. The potassium and water were found by difference.

Experimental Procedure. The experiments were carried out in the following way. Into a solution in equilibrium with two kinds of solid solutions of two salts having a common ion, another salt was added in different proportions and in such an amount that, when the equilibrium was attained, two or three solid phases remained as residue. The mixture in an Erlenmeyer flask of a capacity of about 30 c.c. was made to rotate in a thermostat at 25.0° for at least two days. When the equilibrium was attained, the flask was allowed to stand still in the same thermostat until the suspended matter had settled. Then about 5 c.c. of the solution were taken out by a pipette through a cotton filter into a weighing bottle and subjected to analysis.

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(1) Single salts: Landolt-Börnstein-Roth-Scheel, "Physikalische Tabellen"; Comey, "Dictionary of Chemical Solubilities of Inorganic Compounds"; Seidell, "Solubilities of Inorganic and Organic Compounds." As to the solubility of ammonium chromate at 25° it is 33.62 grams per 100 grams water, according to Araki (*Mem. Coll. Sci. Kyoto Imp. Univ.*, (A) 8, No. 3 (1925)), but the writer has found it to be 39.60.

The system of potassium sulphate, potassium chromate and water: Fock, Seidell's "Solubilities," 2d. ed. p. 559; M. Amadori, "Tables annuelles de constantes et données numériques" 3, 341.

The system of ammonium sulphate, potassium sulphate and water: Fock, Seidell's "Solubilities," 2d. ed. p. 556.

The systems of ammonium chromate, potassium chromate and water, and of ammonium chromate, ammonium sulphate and water: S. Araki, loc. cit.

The composition of the solution was represented by the formula:

$$100m\ H_2O \cdot x(NH_4)_2 \cdot (100-x)K_2 \cdot y(SO_4) \cdot (100-y)CrO_4$$

and it was graphically represented by using a square diagram after E. Janecke.(1)

When it was crystallographically confirmed by a Zeiss polarising microscope that there were two phases in the residue, they were separated from the solution by a centrifugal filter machine and then the two kinds of solid solutions mechanically separated from each other as completely as possible.

The two kinds of residues, each of which contained a little of the other and also some of the mother liquor, were analysed. As the pure residues are anhydrous, the amount of the mother liquor adhereing to them was easily calculated from the amount of water contained in the impure residues. The compositions of the anhydrous impure residues were represented by the formula:

$$x(NH_4)_2 \cdot (100-x)K_2 \cdot ySO_4 \cdot (100-y)CrO_4$$

and plotted in the square diagram. Then the points representing the pure solid phases must lie on the extension of the line connecting the two points. Thus, to find the composition of each of the pure solid phases, the materials were mixed in such calculated proportions that when the equilibrium was reached, the liquid solution of the same composition as above was in equilibrium with only one solid phase having its position on the extension line. When such a mixture attained its equilibrium, the residue was microscopically examined and when the residue was found not to be homogeneous, the experiment was repeated with somewhat modified proportions of the materials. This process was repeated until only one solid phase was detected and then it was taken as one of the solid phases in equilibrium with the given liquid solution.

The results are given in the following table and graphically represented in Fig. 1.

No.	Liquid solution.			Solid solution.			
	m	x	y	A.		B.	
				x	y	x	y
1	9.71	100.00	91.44	100.00	97.10	100.00	78.50
2	10.64	91.51	79.37	73.75	92.29	98.28	11.88
3	12.46	88.12	69.32	42.14	88.89	96.72	11.37
4	14.85	77.30	41.15	24.15	84.93	92.86	9.39
5	14.85	66.05	21.29	21.07	77.32	89.86	7.17
6	15.01	59.51	14.19	17.57	71.66	69.42	6.40
7	15.08	52.04	9.79	37.56	41.41	60.20	9.38
8	15.71	42.61	7.59	37.41	14.61	48.16	7.83
9	15.24	45.17	3.63	—	—	49.76	3.30
10	16.82	61.66	0.00	16.76	0.00	55.50	0.00

---

(1) *Z. anorg. Chem.*, **51** (1906), 132.

The liquid solutions represented by the points on the curve CC′ have always two kinds of solid solutions as the residue which are represented by the points on the lines AA′ and BB′. The crosses on the diagram represent some mixtures of two solid phases and served to find the compositions of the single solid solutions, as above stated.

Fig. 2 represents a model of this system.

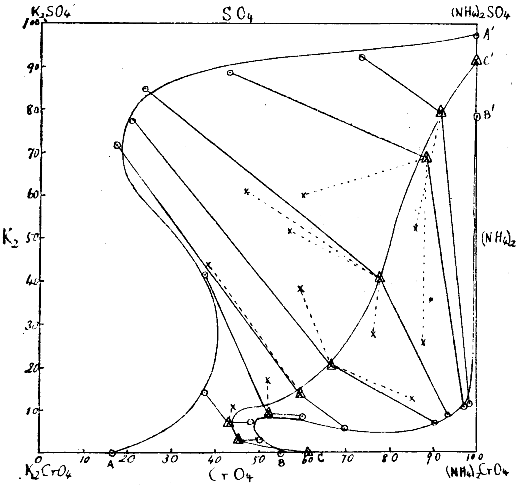

Fig. 1.

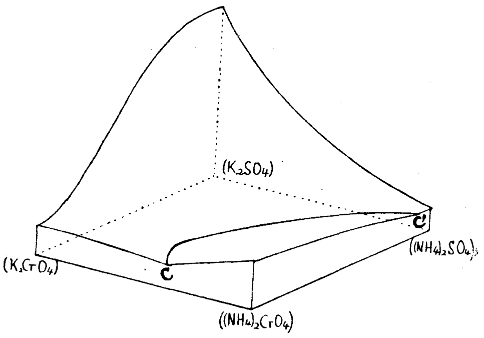

Fig. 2.

Summary.

The equilibrium of the reciprocal salt pair $[K_2, (NH_4)_2]-[SO_4, CrO_4]$ was studied at 25°.

There exist two complete series of solid solutions in equilibrium with liquid solutions.

The compositions of the solid solutions have been determined by a special method.

The equilibrium of the system has been graphically represented using Janecke's square diagram.

In conclusion the writer wishes to express his sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instructions.

Chemical Institute, Faculty of Science,
Kyoto Imperial University.

ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. PART IV. ANOMALOUS DISPERSION AND DEBYE'S DIPOLE THEORY.

By San-ichiro MIZUSHIMA.

Received May 28, 1926. Published July 28, 1926.

A short discussion of the results obtained in the previous experiments[(1)] will be given in the present paper. According to Debye,[(2)] abnormally large values of the dielectric polarization observed in the static field as well as for long electric waves are to be ascribed to the orientation of a molecule which has a permanent dipole in it. The polarization being practically constant for a considerably wide range of frequency, the molecule must adapt itself to the change of the external field and manifest fully its dipole moment when the frequency is not very great. To the rotation of a molecule, however, there must exist a resistance which depends upon the internal friction and the dimension of the molecule. Therefore when the frequency of the external field attains a certain value, the molecule will not have time enough to arrange itself in order to exhibit fully its static moment. This must be the cause of the decrease of dielectric constants observed in the previous experiments. When the frequency is still increased, the molecule can hardly adapt itself to the external frequency and the effect of dipole to the dielectric polarization will almost disappear. This is the case for the value of dielectric constants of glycerine, amyl and isobutyl alcohols observed at lower temperatures.

Debye[(3)] treated this phenomenon theoretically and derived the following equation.

$$\varepsilon=\left\{\frac{\left(\frac{\varepsilon_0}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{\varepsilon_\infty}{\varepsilon_\infty+2}\right)^2}{\left(\frac{1}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{1}{\varepsilon_\infty+2}\right)^2}\right\}^{\frac{1}{2}}\cos^2\frac{\varphi}{2}$$

where

$$\tan\varphi=\frac{\omega\rho}{kT}\,\frac{\varepsilon_0+2}{\varepsilon_\infty+2}\,\frac{1-\frac{\varepsilon_\infty}{\varepsilon_0}}{1+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{\varepsilon_0+2}{\varepsilon_\infty+2}\right)^2\frac{\varepsilon_\infty}{\varepsilon_0}},\quad \rho=8\pi\eta a^3.$$

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(1) This journal, **1** (1926), 47 83 & 115.

(2) Debye, *Physik. Z.*, **13** (1912), 97.

(3) Debye, *Verh. Deut. physik. Ges.*, **15** (1913), 770.

ε is the dielectric constant observed in the alternating field, the frequency of which is $\frac{\omega}{2\pi}$; ε_0 the static dielectric constant; ε_∞ the dielectric constant at the frequency at which the effect of dipole disappears; η the viscosity; a the radius of molecule; T the absolute temperature and k Boltzmann's constant. Among the data necessary for the calculation of ε of monovalent alcohols, ε_0 is known from the study of Abegg and Seitz(1) and ε_∞ from the refractive indices for visible light.(2) The most rational value of a can be obtained by the kinetic theory from the viscosities in the gaseous state. But this method is available only for ethyl alcohol.(3) For homologous series of alcohols a^3 can be assumed to be proportional to b in van der Waals' equation. The values of a for other alcohols can, therefore, be calculated from a for ethyl alcohol and b given in Landolt-Börnstein's Tables.(4) The viscosities of alcohols at low temperatures were recently measured by Mr. Yoshizaki in our institute. Thus we have all data necessary for the calculation of ε. The calculated values of ε ($\varepsilon_{\text{cal.}}$) and those observed at the wave length of 9.5 metres ($\varepsilon_{\text{obs.}}$) are shown in the following tables.

	Ethyl Alcohol $a=1.8\times10^{-8}$ cm.					Propyl Alcohol $a=2.0\times10^{-8}$ cm.				
Temp.	ε_0	ε_∞	η	ε_{cal}	ε_{obs}	ε_0	ε_∞	η	ε_{cal}	ε_{obs}
20	25.8	1.85	0.0119	26	25	22.2	1.92	0.0226	22	22
10	27.0	1.86	0.0145	27	27	23.5	1.94	0.0292	23	23
0	28.4	1.88	0.0177	28	28	24.8	1.95	0.0388	24	25
−10	30.3	1.90	0.0218	30	30	26.2	1.97	0.0513	24	25
−20	32.0	1.91	0.0276	31	31	27.5	1.98	0.0716	22	24
−30	33.7	1.92	0.0358	32	33	29.0	2.00	0.103	19	20
−40	35.3	1.94	0.0490	31	33	30.5	2.02	0.154	14	15
−50	37.6	1.96	0.0684	29	29	32.0	2.03	0.236	9	10
−60	39.7	1.98	0.0959	25	24	33.7	2.05	0.386	6	7

---

(1) Abegg and Seitz, *Z. physik. Chem.*, **29** (1899), 242.

(2) The square of the refractive index for D line were taken as ε_∞, disregarding the inversion of spectrum in the infra-red region.

(3) Landolt-Börnstein "Tabellen" (1923).

(4) b for amyl alcohol can be extrapolated on the assumption that b is additive for homologous series.

	Isobutyl Alcohol $a=2.0\times10^{-8}$ cm.					Amyl Alcohol $a=2.1\times10^{-8}$ cm.				
Temp.	ε_0	ε_∞	η	$\varepsilon_{\mathrm{cal}}$	$\varepsilon_{\mathrm{obs}}$	ε_0	ε_∞	η	$\varepsilon_{\mathrm{cal}}$	$\varepsilon_{\mathrm{obs}}$
20	20.0	1.95	0.0391	19	19	16.0	1.98	0.0437	16	16
10	21.0	1.97	0.0555	20	20	16.8	2.00	0.061	16	18
0	21.8	1.99	0.0804	19	20	17.5	2.02	0.0876	15	17
−10	23.2	2.00	0.116	17	17	18.6	2.03	0.130	13	15
−20	24.5	2.02	0.182	13	11	19.7	2.05	0.207	9	10
—30	25.7	2.03	0.30	8	7	20.8	2.07	0.33	6	7
—40	27.0	2.05	0.56	4	5	21.8	2.08	0.58	4	5
−50	29.0	2.07	1.14	3	4	23.0	2.10	1.01	3	4

It can now be admitted that Debye's theory holds in the first approximation for monovalent alcohols. The discussion on glycerine will be given in the following papers which will also contain the results measured at different wave lengths.

The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

ETUDES DE DÉRIVÉS DU FURFURAL.
II. ETUDES SPECTROGRAPHIQUES DE QUELQUES CÉTONES FURYLIQUES.

Par Itizo KASIWAGI.

Reçu le 11 mai 1926. Publié le 28 juillet 1926.

Dans un premier mémoire(1) nous avons mentionné que nous avions réussi à préparer de nouvelles cétones furyliques. Ces cétones présentent des propriétés optiques très remarquables ; —exaltation de la réfraction moléculaire, comme nous en avons déja signalée, coloration intense à l'action des alcalis, pouvoir absorbant des rayons ultraviolets, etc. C'est l'étude spectrographiques de la relation entre l'absorption et la constitution des cétones.

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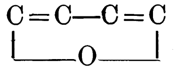
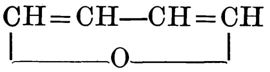
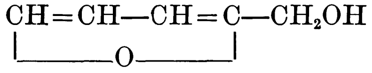
(1) Kasiwagi, Ce journal, **1** (1926), 90.

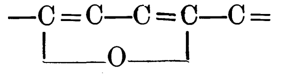
Toutes les cétones étudiées renferment dans leurs molécules au moins un noyau furanique,  $\underset{|\underline{\qquad O \qquad}|}{C=C-C=C}$, qui constitute leur chromophore principale. Ce chromophore semble un faible absorbeur de rayons, car le furfurane  $\underset{|\underline{\qquad\quad O \qquad\quad}|}{CH=CH-CH=CH}$ en solution alcoolique ne donne pas absorption séléctive ni dans la région visible ni dans la région ultraviolette,(1) mais, lorsqu'il est combiné avec un autre chromophore, il devient presque sans exception un chromogène très puissant. Par légère alourdissement de la molécule absorbante, une bande d'absorption apparaît dans la régien ultraviolette. Nous avons pu constater ce fait par le furylcarbinol (I), qui, malgré son faible pouvoir absorbant, donne une bande à $\lambda=267\mu\mu$ environ. Cette absorption n'a lieu qu'en solution assez concentrée (1/10 N), comme on le voit plus loin.

L'absorption du furfural a fait l'objet d'études assez nombreuses. Hartley et Dobbie examinèrent les solutions alcooliques de furfural (aux divers concentrations) et ne purent trouver aucune bande d'absorption.(2) Cependent il est douteux qu'il n' en possède pas de tout, lors même le furylcarbinol (I) absorbe séléctivement.



$$\underset{|\underline{\qquad\quad O \qquad\quad}|}{CH=CH-CH}=C-CH_2OH \qquad (I)$$

En 1910 Purvis étudia l'absorption du furfural à l'état de vapeur et en solution, et trouva que la solution alcoolique à 1/1000 N absorbe près de $\lambda=270\mu\mu$ à l'épaisseur 2 mm. de la couche de la solution.(3) Plus tard Bielecki et Henri étudièrent la même absorption quantitativement, et trouvèrent deux bandes, dont les maxima se trouvent à $\lambda=268\mu\mu$ (bande principale) et à $\lambda=334.5\mu\mu$.(4) Tout récemment Getman a reprit cette étude, et il a constaté que l'aldéhyde possède une bande, dont le maximum se trouve à $\lambda=270\mu\mu$.(5)

Cette bande à $\lambda=270\mu\mu$ environ, est-elle attribuée au noyau furanique seul ou au groupement furfurylidénique  $\underset{|\underline{\qquad O \qquad}|}{-C=C-C=C}-C=$, c'ést-à-dire au noyau furanique plus une double liaison éthylénique (la double liaison entre C et O du groupe carbonyle) en position conjuguée avec une dans le noyau ?

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(1) Purvis, *J. Chem. Soc.*, **97** (1910), 1655.

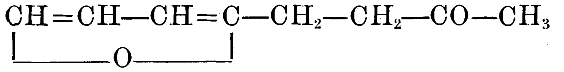
(2) Hartley et Dobbie, *J. Chem. Soc.*, **73** (1898), 598.

(3) Purvis, loc. cit.

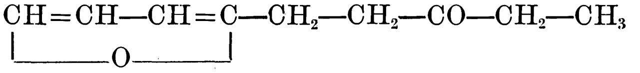
(4) Bielecki et Henri, *Ber.*, **47** (1914), 1690.

(5) Getman, *J. Phys. Chem.*, **28** (1924), 397.

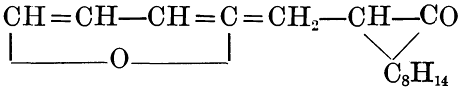
Les cétones furyliques avec une chaine latérale saturée, telles que la furylbutanone (II), la furylpentanone (III) et le furfurylcamphre (IV),



$$CH{=}CH{-}CH{=}C{-}CH_2{-}CH_2{-}CO{-}CH_3 \quad \text{(II)}$$



$$CH{=}CH{-}CH{=}C{-}CH_2{-}CH_2{-}CO{-}CH_2{-}CH_3 \quad \text{(III)}$$



$$CH{=}CH{-}CH{=}C{=}CH_2{-}CH{-}CO \quad \text{(IV)}$$

possèdent une bande exactement en même position, comme suit :

TABLE 1.

	Position du maximum de la bande(1)
Furylbutanone	$\lambda=266\mu\mu$
Furylpentanone	268
Furfurylcamphre	266
Furylcarbinol	268

Dans ces cas, quoique les constitutions des composés cités diffèrent considérablement les unes des autres, ils donnet une bande à la même position $\lambda=267\mu\mu$. Il est tout à fait remarquable que l'alcool renferme le même chromophore que celui du furfurane, et donne une bande à la même position. Par conséquent on peut conclure que le groupe carbonyle des cétones citées, ainsi que celui du furfural, n'influe pas du tout sur la position de l'absorption du noyau furanique.

Cependant le groupement carbonyle présente toujours plus ou moins un effet chromatique. On peut voir ce fait dans la Table 2. (pour construire cette table on calcule de chaque observation, les épaisseurs minima des bandes à la même con-

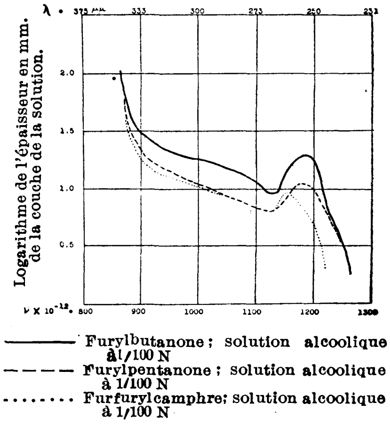


Fig. 1.

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(1) Les valeur sont simplement moyens arithmétiques des longueurs d'onde aux deux extrémités des bandes d'absorption aux épaisseurs les plus minces.

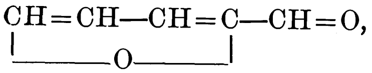
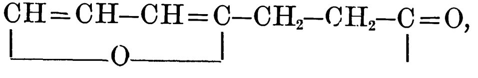
centration dite 1/10000 N d'après la lois de Beer, c'est-à-dire

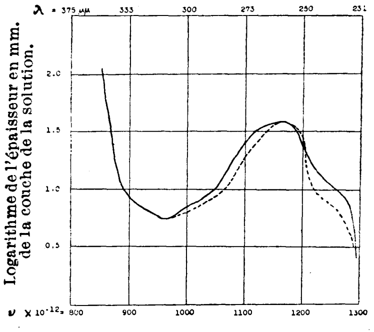
$$c.\ d = \text{constant},$$

où c = concentration et d = épaisseur de la couche de la solution) :

Table 2.

	Epaisseur de la couche la plus mince de chaque solution à 1/10000N où l'absorption paraît.
Furylbutanone	900 mm.
Furylpentanone	700
Furfurylcamphre	700
Furylcarbinol	20000
Furfural	20

Ces chiffres étant naturellement inversement proportionnels aux coéfficients d'absorption, le furylcarbinol est le plus transparent aux rayons ultraviolets, tandis que le furfural est le plus opaque. On peut conclure que, dans le cas du furfural, qui possède deux fois les doubles liaisons conjuguées, en tenant la double liaison intremédiaire en commun  $\underbrace{\mathrm{CH{=}CH{-}CH{=}C}}_{\mathrm{O}}\mathrm{{-}CH{=}O}$, le groupe carbonyle influe fortement sur le noyau furanique, et en cas des cétones furyliques, qui renferment les mêmes chromophores que le furfural, mais le groupe carbonyle est éloigné du noyau furanique, ainsi perdant une double liaison conjuguée  $\underbrace{\mathrm{CH{=}CH{-}CH{=}C}}_{\mathrm{O}}\mathrm{{-}CH_2{-}CH_2{-}C{=}O}$, le même groupement influe assez peu, mais également avec la même intensité.



——— Furylbuténone ; solution alcoolique à 1/10000 N
– – – Furylpenténone; solution alcoolique à 1/10000 N

Fig. 2.

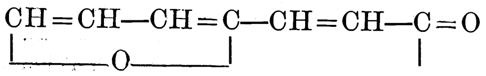
En haut nous avons décrit seulement l'éffet hyperchrome du groupe carbonyle. On peut en voir en bas l'effet hyperchrome et bathochrome à la fois, par introduction d'une double liaison dans les molécules absorbantes entre le groupe carbonyle et le noyau furanique, formant ainsi un système optique puissant  $\underbrace{\mathrm{CH{=}CH{-}CH{=}C}}_{\mathrm{O}}\mathrm{{-}CH{=}CH{-}C{=}O}$ La table suivante montre clairement ce fait :

TABLE 3.

	Position de la bande(1)	Epaisseur minimum de la solution à 1/10000 N où l'absorption paraît.
Furylbuténone(2)	$\lambda = 314 \mu\mu$	6 mm.
Furylpenténone(3)	311	6
Furyldiméthylpenténone(4)	314	7
Furfuralcamphre(5)	314	8

Ces chiffres indiquent que les cétones non saturées déplacent l'absorption maximum bathochromiquement environ $50 \mu\mu$ (c'est-à-dire vers le coté rouge du spectre), et elles absorbent presque 100 fois plus que les cétones saturées correspondentes.

Par cette étude spectrographique nous avons pu constater qu'il existe une relation nette entre l'absorption et la constitution des cétones furyliques.

De plus par augementation du nombre de doubles liaisons l'effet bathochrome se manifeste avec intensité, car la difuryl-1.5-pentadién-1.5-one-3 donne *probablement* deux bandes assez larges. Stobbe et Haertel en ont étudiée l'absorption seulement dans les régions visibles, et conséquemment ils n'ont pas mentionné l'existence des bandes.(6)

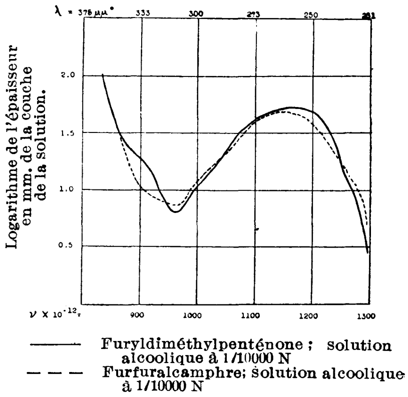


Fig. 3.

Dans la table ci-dessous nous donnerons une comparaison des groupements phényle et furyle :

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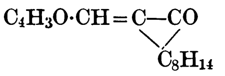
(1) Voir (1) la page 147.

(2) $C_4H_3O \cdot CH = CH \cdot CO \cdot CH_3$

(3) $C_4H_3O \cdot CH = CH \cdot CO \cdot CH_2 \cdot CH_3$

(4) $C_4H_3O \cdot CH = CH \cdot CO \cdot C(CH_3)_3$

(5) 

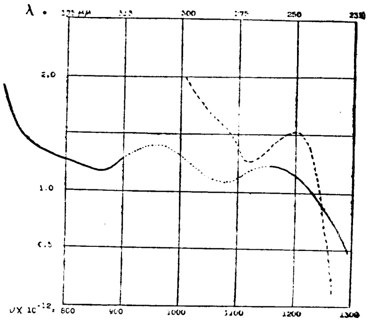
$$C_4H_3O \cdot CH = \underset{\diagdown \; C_8H_{14} \; \diagup}{C - CO}$$

(6) Stobbe et Haertel, *Ann.*, 370 (1909), 99.

TABLE 4.

	Position de la bande	Epaisseur minimum de la solution à 1/10000 N où l'absorption paraît
Benzalcamphre(1)	$\lambda=290\ \mu\mu$	18 mm.
Furfuralcamphre	314	8
Phénylbuténone(2)	285	7.6
Furylbuténone	314	6

On peut y voir nettement que le noyau furanique est, comme Stobbe et Haertel l'ont remarqué en se bornant dans les régions visibles,(3) plus bathochrome et plus hyperchrome que le noyau benzénique, même dans la région ultraviolette.



—— Difurylpentadiénone ; solution alcoolique à 1/10000 N
– – – Furylcarbinol ; solution alcoolique à 1/10 N

Fig. 4.

Note Experimentale.

Les cétones furyliques que nous avons étudiées ont été preparées dans notre laboratoire,(4) et elles sont distillées à nouveau avant emploi.

Furylbuténone : p. é. 110–114° sous 10 mm. On pèse exactement 0.001 molécule-gramme, dissout dans de l'alcool dit "alcool absolu Merck" en faisant en 100 c.c. Ainsi on a la solution alcoolique à 1/100 N. Pour obtenir la solution à 1/10000 N on étend 1 c.c. de cette solution à 100 c.c.

Furylpenténone : p. é. 132–135° sous 20 mm.

Furyldiméthylpenténone : p. é. 145–147° sous 35 mm.

Furfuralcamphre : p. é. 165–180° sous 10 mm. Ce corps est préparé d'après le procédé de Mlle. N. Wolf au moyen de l'amidure de sodium.(5)

Difurylpentadiénone : p. f. 57.5–58.5.°(6)

Furylbutanone : p. é. 81° sous 10 mm.

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(1) Lowry et Southgate, *J. Chem. Soc.*, **97** (1901), 905. Nous avons calculé ces valeurs, en mettant $1/\lambda=3450$ et l'épaisseur de la solution à 1/1000 N=1.8 mm. par interpolation de la courbe donnée par ces auteurs.

(2) Baly et Schaefer, *J. Chem. Soc.*, **93** (1908), 1813. En basant de la courbe donnée, nous avons obtenu $\lambda=235\mu\mu$ et l'épaisseur minimum de la couche de la solution =7.6 mm.

(3) Stobbe et Haertel, loc. cit.

(4) I. Kasiwagi, loc. cit.

(5) Mlle. N. Wolf, *Ann chim.*, (9), **20** (**1923**), 32.

(6) Erdmann, *Ber.*, **35** (1902), 1855.

Furylpentanone : p. é. 88° sous 10 mm.

Furfurylcamphre : p. é. 165° sous 10 mm.⁽¹⁾

Furylméthanol : p. é. 73.5° sous 15 mm. Préparé d'après le procédé de Erdmann.⁽²⁾

Le spectrographe en quartz que nous nous sommes servi est du type E 3 d'Adam Hilger, à Londres, et les plaques photographiques sont l'anti screen, Wellington et Ward.

Comme source lumineuse nous avons employé l'arc entre éléctrodes en fer.⁽³⁾

Pour construire les graphiques ci-joints on porte en abscisses les fréquences (υ) multipliées par 10^{-12} et en ordonnées les épaisseurs en mm. des couches des solutions en échelle logarithmique. En employant υ au lieu de $1/\lambda$, on a la relation suivante entre ces quantités :

$$\upsilon = 3 \times 10^{17}/\lambda$$

où 3×10^{17} est la vitesse de la lumière.⁽⁴⁾

Haute école polytechnique de Yokohama.

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(1) Mlle. N. Wolf, *Ann. chim.*. (9), **20** (1923), 32.

(2) Erdmann, *Ber.*, **35** (1902), 1855.

(3) Nous tenons à remercier bien vivement à M. Y. Shibata, professeur de l'Université de Tokyo, qui a eu l'obligence de nous fournir des éléctrodes.

(4) V. Henri, "Etudes de Photochimie," 1919.

STUDIES ON PROTEINS. III.

ACTION OF SUPERHEATED WATER ON PROTEINS. II.(5)

By Shigeru KOMATSU and Chuichi OKINAKA.

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It has been shown in the previous article(6) on this subject, that proteins when subjected to the action of superheated water, were transformed into soluble and insoluble substances which were regarded as the result of reverse reactions—polymerisation or condensation and hydrolysis—which take place simultaneously in the reaction system, and that these reaction products were different with each individual protein from which they were derived, from the study of the elementary analysis and the distribution of nitrogen,

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(5) The expenses of this investigation were shared by the Imperial Academy of Japan.

(6) This journal, 1 (1926) 102.

which have no definite chemical compositions, according to the various external conditions under which the proteins were submitted to the chemical action.

For the verification of the above conclusions, the present research on the determination of the P_H value and the buffer action of the individual reaction products from proteins at the various stages of the reaction, was undertaken.

TABLE 1.

Edestin.

Time (in hours) (t)	0		1		2		4		20
Diss. subst. (%) (Q)	0		5.7		15.5		24.7		63.4
$\Delta Q/\Delta t$(1)		5.7		9.8		4.6		2.4	
P_H	6.3		7.3		—		—		6.9

Time (in hours) (t)	0		3		6		9
Quantity of diss. amide nitrogen (Q) (%)	0		25.		49.		53.
$\Delta Q/\Delta t$		25		8		1.3	

Gliadin.

Time (in hours) (t)	0		2		6		15.5
Diss. subst. (%) (Q)	0		5.5		9.9		28.8
$\Delta Q/\Delta t$		2.75		1.1		2.	
P_H	5.7		—		6.37		6.44

Casein.

Time (in hours) (t)	0		2		6		17		20
Diss. subst. (%) (Q)	0		1.34		5.85		14.		
$\Delta Q/\Delta t$		0.67		1.1		0.74			
P_H	4.6		—		4.7		—		5.0

For the determination of the P_H value of the reaction products—the residue and solution,— each protein was heated with water in a stoppered bottle at 120° for one, six, and twenty hours, respectively, and the hydrogen ion concentration of the products was studied by the electrometric method as will be seen in the above table.

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(1) ΔQ and Δt denote the difference of Q and t respectively.

The P_H value of the solution from edestin, as may be seen in the table, was increased at the beginning of the reaction and then decreased, whilst that from casein shows a constant increase in the progress of reaction. Although the P_H value in case of gliadin was on the increase with reaction time, which seems apparently to be changed in an analogous manner with that in the case of casein, it should be proper to consider, when we study it precisely, that gliadin behaves toward superheated water partly like edestin and partly like casein, since the rate of increment in the P_H value of the solution from gliadin for a first certain time is greater than that for latter part of the reaction period.

When the P_H value of the reaction products of the proteins was compared with the distribution of nitrogen and especially with their amide nitrogen content (Table 1) it was noticed that some parallelism existed between them, and the vicissitude of the P_H value of the solution with lapse of the reaction time, will be explained well by our hypothes mentioned in the previous article that the compounds containing diamino nitrogen would be transformed partly into those containing the amide nitrogen during the process, and moreover, that the manner in which the protein would be decomposed into fragmentary complex groups, would be a characteristic of the individual protein.

The solution obtained from edestin with water at 120° for twenty hours, having the value of P_H of 6.9, will become cloudy when the P_H of the solution reaches 6 by the addition of acetic acid and the precipitation of a compound vividly took place while the P_H was climbing from 5.3 to 5.0 and completed at P_H of 4.8, accordingly the isoelectric point of the substance was assumed to be $P_H=5.2$, since at that point the affinity of a compound for water is in a relative minimum.(1) The same was noticed with the solution ($P_H=6.4$) which obtained by digestion of gliadin with water for twenty hours; when acetic acid was added gradually to the solution, and the precipitation of a compound occurs when the acidity of the solution has reached to $P_H=6.4$, the vicissitude of its isoelectric point. No flocculation, however, has occurred of the solution of the P_H of 5.0, which was prepared from casein under the same conditions as the other proteins, owing to the P_H of the solution being already on the acid side of the isoelectric point of compounds which were regarded as being formed as cleavage products of the casein molecule, and consequently the so-called residue was considered partly of these cleavage products which remained there, without entering into the solution.

From these facts, we concluded that the constituents of the solutions resulting from the action of the superheated water on proteins, would be as different essentially from each other, as the difference of the individual pro-

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(1) W. M. Clark, "The Determ. of Hydrogen Ion Conc." 2nd. ed. (1923), p. 342.

teins in the chemical constituents, which has already been admitted by chemists.(1) Accordingly, the following statement will be borne in mind that the constituents of the insoluble residue, from the study of the P_H value of the soluble substances, would be different from each other, as we stated in the previous article, since the hydrogen ion concentration of a solvent is one of the most important factors controlling the solubility of proteins or amphotelytes of complex nature.(2)

A solution from 2 grams of edestin, by digesting with 40 c.c. of water at 120°, for one hour, and made up to 50 c.c., which was found to have a value of P_H of 7.4. To the solution were added a successively increasing amount of N/25 acetic acid on the one hand, and N/50 sodium hydroxide solution on the other, and the resulting P_H was measured in each case. The P_H values were then plotted as usual and the results were as may be seen in Curve III, in Fig. 1 and Fig. 2. Curve II′, in these figures, was constructed analogously with data obtained with the solution prepared from the protein after digesting for twenty hours under the same conditions. Curve II of the figure were obtained in a similar way of ten times diluted solution of the latter solution. The results show that the buffer action of the solution as we expected from other examples, depended upon the concentration of the constituents. The solution obtained by digestion for twenty hours is much more resistant to change in the P_H than the solution of the same concentration, obtained by digestion for only one hour. These relations were observed to be true also of casein, as will be seen in Fig. 5 and Fig. 6, but of the solution from gliadin, these stochiometrical relations do not hold ; the solutions of the same concentration show the same buffer action though they were prepared under different conditions (Fig. 3 and Fig. 4). That the P_H value of the solution from edestin was decreased from 6.96 to 6.78 when diluted ten times, whilst of its hundred times diluted solution the P_H value was inversely increased to 8.07, are facts worth discussing.

For obtaining more definite knowledge of the occurrence of compounds of complex nature such as albumose or peptone, in the solution which was resulted by digestion of protein, the buffer value of the solution was investigated.

As was supposed from the study of the buffer values (dB/dP_H) of the solutions, differentiated graphically from their titration curve above-mentioned, following the method proposed by D.D. van Slyke,(3) there occur at least two compounds of complex nature in each solution, as will be seen in Fig. 7, 8, 9, 10, 11 and 12, obtained by the action of superheated water on proteins. Such indication of the buffer value for the existence of the compounds will be proved experimentally in the next article by isolating them from the solution.

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(1) T. B. Osborne, "The Vegitable Proteins," (1909), p. 59.

(2) Robertson, "Physical Chemistry of Proteins," (1918), pp. 275, 248.
J. Loeb, "Proteins and the Theory of Colloidal Behavior," pp. 243, 266.
L. Michaelis, "Die Wasserstoffionen-Konzentration," (1919), p. 44.
R. H. Bogue, "Colloidal Behavior." (1924), p. 35.

(3) *J. Biol. Chem.*, 52 (1922), 524.

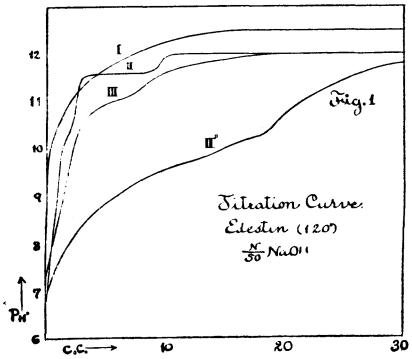

Fig. 1. I: Water.
II: Hydrolized 20 hours (0.25%).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

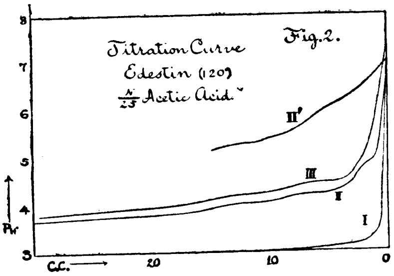

Fig. 2. I: Water.
II: Hydrolized 20 hours (0.25%).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

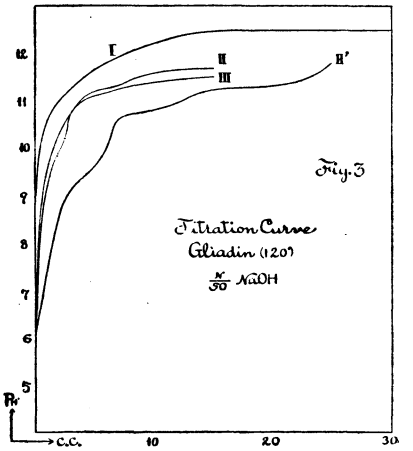

Fig. 3. I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4).

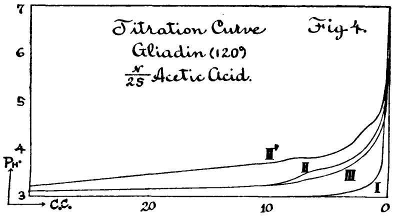

Fig. 4. I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4%).

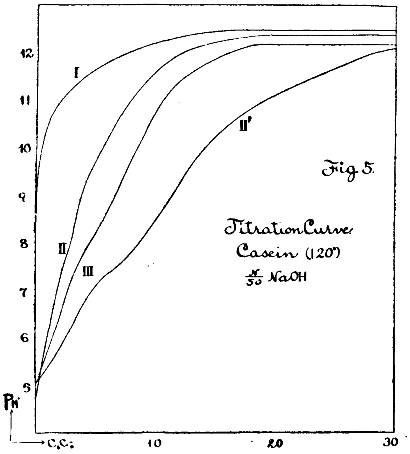

Fig. 5. I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

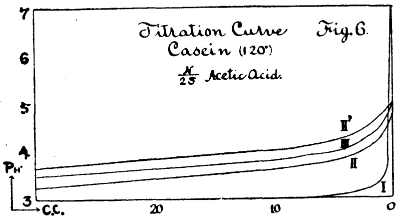

Fig. 6. I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

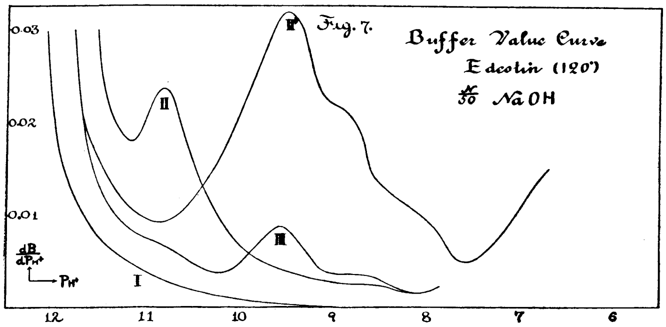

Fig. 7.

I: Water.
II: Hydrolized 20 hours (0.25%).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

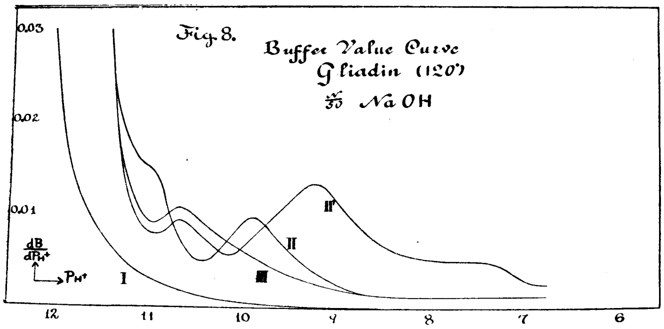

Fig. 8.

I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4%).

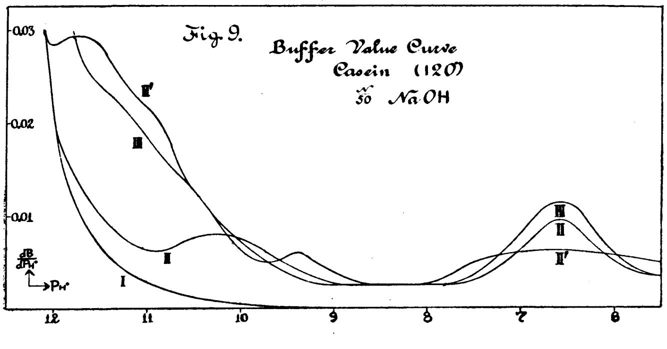

Fig. 9.

I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

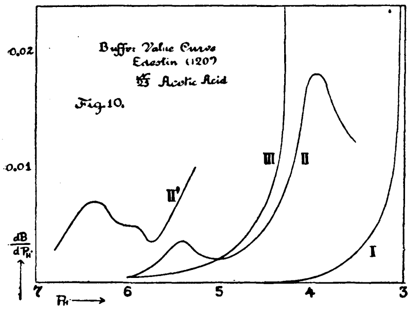

Fig. 10.

I: Water.
II: Hydrolized 20 hours (0.25).
II': Hydrolized 20 hours (2.5%).
III: Hydrolized 1 hour (0.24%).

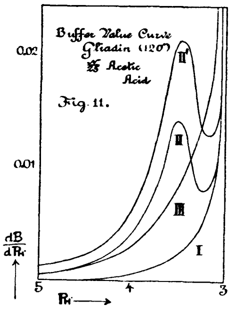

Fig. 11.

I: Water.
II: Hydrolized 20 hours (0.4%).
II': Hydrolized 20 hours (1.4%).
III: Hydrolized 6 hours (0.4%).

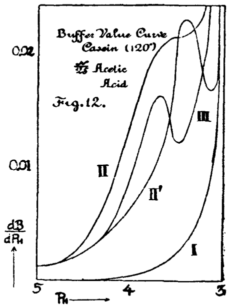

Fig. 12.

I: Water.
II: Hydrolized 20 hours (0.24%).
II': Hydrolized 20 hours (0.64%).
III: Hydrolized 6 hours (0.24%).

November 1924.

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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. I. THE ACTION ON A MIXTURE OF ANILINE AND METHYL ALCOHOL.

By **Harushige INOUE.**

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It has already been shown by Mailhe and Godon,⁽¹⁾ and Brown and Emmet⁽²⁾ that silica and alumina which are the principal components of Japanese acid earth, promote the dehydration of alcohols and also the condensation of alcohols and amines. On repeating these experiments with alumina prepared from ammonium alum obtained from Potter's clay by heating at 700–800° and then treated with concentrated sulphuric acid and ammonium sulphate successively, the same experimental result as obtained by other chemists, was obtained.

When, however, silica, prepared from natural pumice by treating with concentrated nitric acid for several days, and composed of 98.30 percent of

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(1) Mailhe and Godon, *Compt. rend.* **160** (1918), 467 & 564.

(2) Brown and Emmet, *J. Am. Chem. Soc.*, **46** (1924), 1836.

SiO_2 and 1.67 percent of Fe_2O_3, was used as catalyst, a result was obtained which differed from others in detail. A mixture of 46 grams of aniline and 18 grams of methyl alcohol was passed over the catalyst heated at 350°, 47.1 grams of reaction product was obtained, which after examination of the physical constants and the melting point of the acetates of fractions yielded by fractional distillation, as will be seen in Table 1, was confirmed as composed of p-toluidine and methylaniline.

TABLE 1.

No.	Fraction	Yield (gr.)	Sp.gr.(d_{20}^{20})	M.p. of acetate	Principal product
1	90–100°	0.9	—	—	—
2	185–190°	2.9	0.9937	107–111°	Aniline & Methylaniline
3	190–195°	18.1	0.9910	120–122°	Methylaniline & p-toluidine
4	195–198°	6.2	0.9865	124.5–126.5°	Methylaniline & p-toluidine
5	198–202°	4.0	0.9809	132.5–133.8°	p-Toluidine
6	202–210°	2.6	—	129–132°	—
7	210–215°	1.5	—	—	—

p-Toluidine was isolated in the pure form of the acetate (m. p. 146°–147°), from the fifth fraction, b. p. 198–202° shown in Table 1.

The author has, therefore, studied the action of Japanese acid earth on a mixture of methyl alcohol and aniline, and has observed that the condensation of these substances, and the contact isomerisation of the condensed substance have occurred simultaneously.

The catalyst used in the experiment was obtained from crude Japanese acid earth, washed with water, and dried, which gave on analysis the following chemical compositions:

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Moisture dried at 110°	Ignition loss	Total
61.67%	12.28%	1.87%	0.16%	3.44%	15.66%	4.64%	99.72%

The earth was filled in a glass tube of 1 metre in length, and 2 cm. in diameter, heated to 350°, and a mixture of methyl alcohol and aniline was passed on it.

p-Toluidine.

From the reaction product of 22 grams methyl alcohol and 55 grams aniline, 50.4 grams of an oily substance and 17.5 grams of water were obtained, and the oily substance was divided into the following 7 fractions by fractional distillation, and the density of each fraction was determined and the melting-point of the acetates obtained by treating the oil with acetic anhydride was also determined.

TABLE 2.

No.	Fraction	Yield (gr.)	Sp. gr. (d_{20}^{20})	M.p. of acetate	
				1	2
1	to 180°	2.9	—	—	—
2	189-193°	7.4	0.9977	120-121°	about 125°
3	193-197°	13.4	0.9947	139-143°	140-143°
4	197-200°	11.2	0.9904	140-143°	140-143°
5	200-205°	5.0	0.9858	140-143°	103-106°
6	205-207°	3.3	0.9814	114-116.5°	105-106°
7	Residue	2.8	—	—	—

In the table, acetate 1 and acetate 2 respectively show the melting-point of the first and second crops of crystals, separated from solutions.

The third and fourth fractions which composed the main part of the reaction product, from the melting-point of the acetates, were noticed to be composed principally of p-toluidine. Higher fractions boiling above 200°, should contain, by refering to their physical and chemical properties, some homologous substances of aniline, and other secondary and tertiary amines.

Methylaniline.

When, however, a mixture of 50 grams methyl alcohol and 120 grams aniline was passed in an interval of 8 hours on the catalyst heated to 250°, 106 grams of an oily reaction product and 26 grams of water were obtained, and the reaction product was divided into the following 6 fractions by fractional distillation.

TABLE 3.

No.	Fraction	Yield (gr.)	Sp. gr. (d_{20}^{20})
1	75-100°	—	—
2	180-187°	21.7	1.0051
3	187-190°	25.8	1.0028
4	190-197°	37.8	0.9949
5	197-200°	6.1	0.9852
6	Residue	—	—

The fourth fraction, b. p. 190–197°, was confirmed as consisting of methylaniline, since its density and the melting-point of the acetate agree with those of methylaniline.

To our interest, when an equimolecular mixture of methyl alcohol and aniline was passed on Japanese acid earth heated at 250°, methylaniline was obtained as a main reaction product, while the same mixture by the contact action of the same catalyst at higher temperature such as 350°, was noticed to be transformed into p–toluidine which was usually regarded as resulting from methylaniline by Hofmann reaction, and such transformation could not be observed to occur previously when alumina was used as the catalyst. In order to test whether the Hofmann reaction would occur actually by passing a mixture of aniline and methyl alcohol on the heated acid earth, 50 grams of the fourth fraction, b.p. 190–197°, shown in Table 3, which was composed of methylaniline, were passed again on the catalyst heated at 350°, and the reaction product was divided into the following 7 fractions, and the density of each fraction and the melting-point of the acetate, were studied, and also the primary amine-content by means of benzene sulphonylchloride.

TABLE 4.

No.	Fraction	Yield (gr.)	d^{20}_{20}	M.p. of acetate			RNH$_2$ %	N %
				1	2	3		
1	185–187°	5.5	0.9800	113–116°	96°	96–98°	—	9.50
2	187–190°	9.0	1.0050	119–122°	107–111°	96–98°	88.94	9.44
3	190–193°	2.3	1.0050	117–119°	96–98°	83–86°	96.04	9.21
4	193–198°	7.2	1.0023	119–121°	98–100°	70–72°	92.94	9.24
5	198–202°	10.4	1.0000	121.5–124°	101–103°	99–101°	86.90	9.56
6	202–208°	3.0	0.9951	126–129°	115–118°	83–86°	87.30	9.48
7	about 208°	—	—	128–131°	120–122°	91–94.5°	—	—
	p–toluidine	—	—	—	—	—	—	9.39
	aniline	—	—	—	—	—	—	10.37

The fractions 2, 3, 4, 5, and 6 were confirmed from their physical and chemical properties, as consisting mainly of p–toluidine, and the writer has succeeded in obtaining it in pure state as an acetate (m.p. 147°; N=9.40%) from the fifth fraction by fractional crystallisation. And analogously, the first and last two fractions were confirmed to contain chiefly of aniline and dimethylaniline respectively.

The writer, thus, has proved experimentally the assumption that methylaniline formed by the direct condensation of methyl alcohol and aniline, was transformed into p–toluidine by contact action of the acid earth at higher temperature, with the formation of aniline and dimethylaniline.

The mechanism of the reaction for the formation of p–toluidine and dimethylaniline by the interaction of methyl alcohol and aniline in presence of the catalyst will be explained by the following scheme :

$$CH_3OH + C_6H_5NH_2 \longrightarrow C_6H_5NHCH_3 \longrightarrow CH_3C_6H_4NH_2 \cdots\cdots(1)$$

$$C_6H_5NH(CH_3) \longrightarrow C_6H_5NH_2 + C_6H_3N(CH_3)_2 \cdots\cdots\cdots\cdots\cdots\cdots(2)$$

Dimethylaniline which occurs in the reaction product of methylaniline by the contact action, and of aniline and methyl alcohol in presence of the acid earth, should behave in an analogous way yielding methyl–p–toluidine, methylaniline and xylidines, with methylaniline, by the contact action of the catalyst at high temperature.

70 grams of dimethylaniline which contains 4.7% of methylaniline as an impurity, were passed on the catalyst heated at 350°, and a reaction product composed of 35% of primary amines, 28% of secondary amines, and 37% of tertiary amines, was obtained which was divided into 9 fractions by distillation. Of each fraction, the density, content of primary amines, melting point of acetates and content of nitrogen were determined, and the results are shown in the following table.

TABLE 5.

No.	Fraction	Yield (gr.)	d^{20}_{20}	$R-NH_2$ %	M.p. of acetate		Content of N %	
					1	2	1	2
1	140-195°	1.0	—	—	—	—	—	—
2	195-198°	7.0	0.9765	42.70	—	122-124°	9.05	—
3	198-201°	10.0	0.9749	40.98	130-131°	125-128°	9.14	—
4	201-203°	11.0	0.9746	39.42	138-141°	124-127°	9.29	8.77
5	203-205°	17.0	0.9734	37.84	134-135°	130-133°	9.29	8.11
6	205-207°	12.0	0.9704	31.43	139-142°	129-130°	9.16	8.27
7	208-210°	4.0	0.9686	27.26	138-141.5°	129-134°	9.28	7.90
8	211-215°	2.0	0.9686	—	94-96°	—	7.59	—
9	215-225°	2.0	—	—	103-105°	—	—	—

Content of nitrogen in the acetate of C_7H_9N ························ 9.39%
„ „ „ „ „ $C_8H_{11}N$ ························ 8.58%

As will be seen in the experimental results shown in the table above, p–toluidine and methyl–p–toluidine composed chiefly the reaction product, and the chemical reactions for the formation of these compounds from dimethylaniline will be shown in an analogous manner to the transformation of methylaniline into p–toluidine and other amines.

The migration of the methyl radical in both the methyl- and dimethylanilines, from the nitrogen atom to the carbon atom, forming p-toluidine and methyl-p-toluidine, was effected by the contact action of Japanese acid earth, and such chemical change was found with silica but not with alumina, the both were considered to be principal constituents of Japanese acid earth.

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ON THE ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES. PART V. ANOMALOUS DISPERSION AND DEBYE'S DIPOLE THEORY (CONTINUED).⑴

By San-ichiro MIZUSHIMA.

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Electric waves of the wave lengths of 3.08 metres and 50 metres were generated. Measurements of dielectric constants and absorptions were carried out according to the method described in Part II of the present report⑵. The experimental results were interpolated and the values at every ten degrees of temperature are shown in the following tables.

$\varepsilon_{\text{obs.}}$: Dielectric constant,
ε_0 : Static dielectric constant,
ε_∞ : Square of the index of refraction for visible light (D line),
K : Electric conductivity which is equivalent to anomalous absorption (cm.$^{-1}$ ohm^{-1}),
η : Viscosity.

TABLE 1.

Ethyl alcohol

$a=1.8\times10^{-8}$ cm.

Temp.	η	ε_0	$\lambda=50$ m.			$\lambda=3.08$ m.			ε_∞
			$\varepsilon_{\text{calc.}}$	$\varepsilon_{\text{obs.}}$	$K\times10^5$	$\varepsilon_{\text{calc.}}$	$\varepsilon_{\text{obs.}}$	$K\times10^5$	
60°	—	—	—	—	—	—	20	3	—
50	—	—	—	—	—	—	21	4	—
40	—	—	—	—	—	—	22.5	5	—
30	—	—	—	23.5	< 1.0	—	23.5	8	—
20	0.0119	25.8	26	25	〃	25	25	13	1.85
10	0.0145	27.0	27	26.5	〃	26	26.5	21	1.86
0	0.0177	28.4	28	28	〃	26.5	28	32	1.88
−10	0.0218	30.3	30	29.5	〃	26.5	28	49	1.90
−20	0.0276	32.0	32	31.5	〃	25.5	26	72	1.91
−30	0.0358	33.7	34	33	〃	23	21.5	80	1.92
−40	0.0490	35.3	35	35	〃	18	17.5	80	1.94
−50	0.0684	37.6	37	37	〃	13	13.5	67	1.96
−60	0.0959	39.7	39	39	1.2	9	9	47	1.98

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(1) Details of these papers will appear in near future in the *Journal of the Faculty of Science, Imperial University of Tokyo.*

(2) Mizushima, this journal, 1 (1926), 83.

TABLE 2.

Propyl alcohol

$a=2.0\times10^{-8}$ cm.

Temp.	η	ε_0	$\lambda=50$ m.			$\lambda=3.08$ m.			ε_∞
			$\varepsilon_{\text{calc.}}$	$\varepsilon_{\text{obs.}}$	$K\times10^5$	$\varepsilon_{\text{calc.}}$	$\varepsilon_{\text{obs.}}$	$K\times10^5$	
60°	—	—	—	—	—	—	17	3	—
50	—	—	—	17	< 1.0	—	18	5	—
40	—	—	—	18.5	〃	—	19	8	—
30	—	—	—	20	〃	—	20	12	—
20	0.0226	22.2	22	21.5	〃	20	20.5	21	1.92
10	0.0292	23.5	23	23	〃	19	20	34	1.94
0	0.0388	24.8	25	24	〃	17	17.5	48	1.95
−10	0.0513	26.2	26	25.5	〃	14	14	58	1.97
−20	0.0716	27.5	27.5	27.5	〃	10.5	11	50	1.98
−30	0.103	29.0	28.5	29	〃	7	8	34	2.00
−40	0.154	30.5	29	30	1.2	5	6.5	22	2.02
−50	0.236	32.0	27.5	29	2.7	3.5	5.5	14	2.03
−60	0.386	33.7	22.5	24	4.8	3	5	9	2.05

TABLE 3.

Isobutyl alcohol

$a=2.0\times10^{-8}$ cm.

Temp.	η	ε_0	$\lambda=50$ m.			$\lambda=3.08$ m.			ε_∞
			$\varepsilon_{\text{calc.}}$	$\varepsilon_{\text{obs.}}$	$K\times10^5$	$\varepsilon_{\text{calc.}}$	$\varepsilon_{\text{obs.}}$	$K\times10^5$	
60°	—	—	—	—	—	—	14	3	—
50	—	—	—	16	< 1.0	—	15	6	—
40	—	—	—	17	〃	—	16	10	—
30	—	—	—	18.5	〃	—	16.5	18	—
20	0.0391	20.0	20	19.5	〃	15.5	16	29	1.95
10	0.0555	21.0	21	21	〃	13	13	39	1.97
0	0.0804	21.8	22	22	〃	10	10	42	1.99
−10	0.116	23.2	23	23.5	〃	7	6.5	35	2.00
−20	0.182	24.5	23.5	24	1.3	4.5	4.5	17	2.02
−30	0.30	25.7	22.5	23.5	2.6	3	4	7	2.03
−40	0.56	27.0	17.5	18.5	4.1	2.5	3.5	4	2.05
−50	1.14	29.0	10	10	4.0	2	3	3	2.07
−60	—	—	—	6	2.6	—	3	2	—

TABLE 4.

Amyl alcohol

$a = 2.1 \times 10^{-8}$ cm.

Temp.	η	ε_0	$\lambda = 50$ m.			$\lambda = 3.08$ m.			ε_∞
			$\varepsilon_{\text{calc}}$,	$\varepsilon_{\text{obs.}}$	$K \times 10^5$	$\varepsilon_{\text{calc.}}$	$\varepsilon_{\text{obs.}}$	$K \times 10^5$	
60°	—	—	—	—	—	—	12	3	—
50	—	—	—	—	—	—	13	5	—
40	—	—	—	—	—	—	13.5	9	—
30	—	—	—	—	—	—	13.5	17	—
20	0.0437	16.0	16	15	< 1.0	13	13	26	1.98
10	0.061	16.8	17	16.5	〃	10.5	10.5	33	2.00
0	0.0876	17.5	17.5	17.5	〃	7.5	7.5	30	2.02
−10	0.130	18.6	18.5	18.5	〃	5.5	5.5	20	2.03
−20	0.207	19.7	18.5	19	1.0	4	4	10	2.05
−30	0.33	20.8	18	17.5	2.2	3	3.5	4	2.07
−40	0.58	21.8	14	13	3.6	2.5	3	3	2.08
−50	1.01	23.0	9	8	3.0	2	3	2	2.10
−60	—	—	—	5.5	1.7	—	3	2	—

TABLE 5.

Glycerine

Temp.	ε $\lambda = 1000$ m. (Graffunder)	$\lambda = 50$ m.		$\lambda = 3.08$ m.		ε $\lambda = 1.36$ m. (Bock)
		$\varepsilon_{\text{obs.}}$	$K \times 10^5$	$\varepsilon_{\text{obs.}}$	$K \times 10^5$	
60°	36	—	—	—	—	35
50	38	37	< 1.0	40	36	36
40	39	39	〃	40.5	58	33
30	41	40.5	〃	38	90	25
20	43	43	〃	28.5	95	14
10	45	44	2.0	14	55	5
0	47	36	4.0	9	30	3.5
−10	—	23	5.6	7	14	3
−20	—	13	2.4	5	6	3
−30	—	8	< 1.0	4.5	3	3
−40	—	6	〃	4	< 2	3
−50	—	5	〃	3.5	〃	3
−60	—	4.5	〃	3	〃	3

The variation of dielectric constants and absorptions due to temperature observed at a constant wave length is, in general, quite analogous to that for the wave of 9.5 metres (see Part II and III).(1)

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(1) Mizushima, this journal, **1** (1926), 83 & 115.

The values of ε at higher temperatures are independent of wave length and equal to those for static field even for the wave length of 3.08 metres. As the temperature is gradually lowered, the absorption of wave becomes stronger and ε undergoes a great change at a certain wave length. For instance at $-20°$, ε of amyl alcohol for the wave length of 50 metres is 19, a value not far from the static dielectric constant, then ε decreases to 4, a value approaching to the square of the refractive index for the visible light (N_v^2). At still lower temperatures e.g. at $-60°$ where the absorption of wave again decreases, all the values of ε for different wave lengths approach to one another and are not far from N_v^2. This was not observed for ethyl alcohol, but if the experiment could be carried out at sufficiently low temperatures, liquid ethyl alcohol would also show this end of anomalous dispersion.

In short the dielectric constants of alcohols and glycerine change continuously from the large value for the static field to the small value nearly equal to N_v^2 and the region of anomalous dispersion accompanying intense absorption shifts to longer wave lengths as the temperature is lowered.

Here we have a relation between the anomalous dispersion and absorption of electromagnetic waves, which is quite analogous to that for the visible light. But it should be noticed that an absorption band in the visible as well as in the infra-red or ultra-violet parts is not so much effected by the temperature variation, while a band in the electric spectrum undergoes an enormous effect and the band shifts to the longer wave lengths as the temperature is lowered. From the measurement of the anomalous electric absorption by Drude,(1) the wave length of 70 cm. is often adopted, without the indication of temperature, as the characteristic wave length of alcohols, but when the absorption band in the electric spectrum is considered, the indication of temperature must not be forgotten as is shown above.(2)

As to the anomalous absorption for a definite wave length, Drude noticed in his paper that the absorption by alcohols becomes stronger as the temperature is lowered. However, such is the case only at comparatively higher temperatures. As the temperature is lowered, the absorption reaches a maximum, then decreases till it almost disappears. It is evident that all of the Drude's experiments were carried out at the temperatures higher than that for this maximum absorption.

Now the above results can be discussed from the view-point of Debye's dipole theory, of which a short explanation was already given in Part IV.(3)

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(1) Drude, *Z. physik. Chem.*, **23** (1897), 267.
(2) Landolt-Börnstein's "Tabellen," (1923), p. 807.
(3) Mizushima, this journal **1** (1926), 143.
Debye, *Verh. Deut. Physik. Ges.* **15** (1913), 770.

The distribution function of dipole axes for the angle θ under the periodic force $Ke^{i\omega t}$ is

$$F=A\left(1+\frac{1}{1+\frac{i\omega\rho}{kT}}\ \frac{m}{kT}\ Ke^{i\omega t}\cos\theta\right)\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where

$$\rho=8\pi\eta a^3$$

and A is a constant, η the viscosity, a the radius of the molecule, m the moment of dipole, k Boltzmann's constant and T the absolute temperature.

This becomes for a static field :

$$F_0=A\left(1+\frac{m}{kT}\ K\cos\theta\right)\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

The difference in the distribution between a static and an alternating field is, therefore, determined by the expression $\left(1+\frac{i\omega\rho}{kT}\right)$, in which

$$\frac{\rho}{kT}=\frac{8\pi\eta a^3}{kT}=\tau\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

expresses the time of relaxation of the molecule. So long as the period of external field is very great as compared with τ, the distribution of the dipole axes will remain practically constant. Consequently the dielectric polarization is independent of wave length and equal to that for the static field. If, however, the external period approaches to the time of relaxation, F becomes different from F_0 and the medium will show anomalous dispersion. We see in equation (3) that the value of τ is proportional to the viscosity η and the cube of the molecular radius a^3 and inversely proportional to the absolute temperature T. Therefore the anomalous region will shift to the longer wave lengths as the temperature is lowered and the viscosity becomes greater. The effect will be the same as we proceed from lower to higher alcohols, because the molecular radius as well as the viscosity becomes greater. These are all what are confirmed by the above experiments.

From equation (1) we can calculate the dielectric constant ε for an alternating field of the frequency $\frac{\omega}{2\pi}$,

$$\varepsilon=\left\{\frac{\left(\frac{\varepsilon_0}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{\varepsilon_\infty}{\varepsilon_\infty+2}\right)^2}{\left(\frac{1}{\varepsilon_0+2}\right)^2+\frac{\omega^2\rho^2}{k^2T^2}\left(\frac{1}{\varepsilon_\infty+2}\right)^2}\right\}^{\frac{1}{2}}\cos^2\frac{\varphi}{2}$$

where

$$\tan\varphi=\frac{\omega\rho}{kT}\,\frac{\varepsilon_0+2}{\varepsilon_\infty+2}\,\frac{1-\dfrac{\varepsilon_\infty}{\varepsilon_0}}{1+\dfrac{\omega^2\rho^2}{k^2T^2}\left(\dfrac{\varepsilon_0+2}{\varepsilon_\infty+2}\right)^2\dfrac{\varepsilon_\infty}{\varepsilon_0}}$$

The values of $\varepsilon_{\text{calc.}}$ are calculated for the wave length of 3.08 metres and 50 metres according to the method as explained in Part IV⁽¹⁾ and are compared with the observed values ($\varepsilon_{\text{obs.}}$). As shown in the above tables, $\varepsilon_{\text{calc.}}$ agrees pretty well with $\varepsilon_{\text{obs.}}$

For glycerine we have no data for a. Therefore no systematic discussion can be made. If, however, we take at 18° the value of ε_0 equal to 43 (Graffunder⁽²⁾), that of η to 10.69 (Jones⁽³⁾), that of ε_∞ to 2 and that of $\varepsilon_{\text{obs.}}$ to 25.5 (present experiment), then we obtain the following value of a for glycerine :

$$a=2.8\times10^{-9}\text{ cm.}$$

This is not a reasonable value, because the molecular radius is of the order of 10^{-8} cm. even for simple diatomic molecules and that for a complex molecule such as glycerine must be greater than this. We must, therefore, agree with Bock⁽⁴⁾ that Debye's formula does not hold for glycerine. As the viscosity of glycerine is abnormally great, it is very doubtful whether η in the resistance term $8\pi\eta a^3$ is equivalent to the mass viscosity of glycerine. If glycerine be a colloidal system and its mass viscosity must be considered as the viscosity of heterogeneous mixture,⁽⁵⁾ the effective viscosity acting on the rotation of a molecule will be quite different from ordinary viscosity. Then we can naturally consider the glycerine to be an exception for Debye's theory.

Allowing this exception, the result of the author's experiment may be considered to be the first experimental evidence of the dipole theory on the anomalous dispersion of electric waves.

The author wishes to express his best thanks to Prof. M. Katayama for his kind guidance.

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(1) Loc. cit.

(2) Graffunder, *Ann. Physik.* **70** (1923), 225.

(3) Jones, *Phil Mag.*, (5) **37** (1894), 451.

(4) Bock, *Z. Physik*, **31** (1925), 534.

(5) Einstein, *Ann. Physik*, **19** (1906), 289.

THERMODYNAMIC STUDIES ON ZINC IODIDE AND MERCUROUS IODIDE.(1)

By Fusao ISHIKAWA and Eiichi SHIBATA.

Received June 29, 1926. Published August 28, 1926.

I. The Fictitious Heat of Solution of Zinc Iodide. As is well known, the fictitious heat of solution of an anhydrous salt can be determined by the following thermodynamic relations, existing between the temperature coefficients of the electromotive forces, $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$, of the reversible cells with and without solid salt.(2)

$$(Q)_T = T\left[\left(\frac{dE}{dT}\right)_A - \left(\frac{dE}{dT}\right)_B\right] n \cdot 23074 \cdots\cdots (1)$$

$$(Q)_T = T\left(\frac{dE}{dC}\right)_T \left(\frac{dC}{dT}\right) n \cdot 23074 \cdots\cdots\cdots\cdots\cdots (2)$$

The authors have determined the fictitious heat of solution of zinc iodide with the aide of formula 1. In the case of zinc iodide, formula 2 is not suitable for this purpose, owing to the experimental difficulties in determining the temperature coefficient of solubility of zinc iodide as it has been known to be exceedingly small.

The following cells were constructed and their electromotive forces were measured at several temperatures, the results are shown in tables 1 and 2.

Zn amalgam 10% | Zinc iodide, saturated solution, Hg_2I_2 solid salt | Hg······Cell A.

Zn amalgam 10% | Zinc iodide, saturated solution, Hg_2I_2 | Hg······Cell B.

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(1) This is the abstract of a paper which will be published in *The Science Reports of the Tôhoku Imperial University.*

(2) E. Cohen, and others, *Z. Physik. Chem.* **93**, (1918), 43; **94**, (1920), 210; **105**, (1923), 155.

Table 1.

Cell A, with solid salt.

Temperature degree	Electromotive forces		
	Observed (mean) volt	Calculated volt	Calc.—obs.
20.00	0.52358	0.52358	0.00000
22.50	0.52391	0.52395	+0.00004
25.00	0.52429	0.52429	0.00000
27.50	0.52461	0.52462	+0.00001
30.00	0.52489	0.52492	+0.00003
32.50	0.52519	0.52521	+0.00002
35.00	0.52551	0.52548	−0.00003

Table 2.

Cell B, without solid salt.

Temperature degree	Electromotive forces		
	Observed (mean) volt	Calculated volt	Calc.—obs.
20.00	0.52278	0.52300	+0.00022
22.50	0.52350	0.52356	+0.00006
25.00	0.52415	0.52415	0.00000
27.50	0.52478	0.52477	−0.00001
30.00	0.52543	0.52543	0.00000
32.50	0.52612	0.52612	0.00000
35.00	0.52685	0.52685	0.00000

By the method of least square the following equation was obtained for the cell A and the electromotive forces calculated are given in the third column of Table 1.

$$E = 0.52429 + 0.0001336\,(t-25) - 0.000001496\,(t-25)^2$$

which gives

$$\left(\frac{dE}{dT}\right)_{A,\,298} = 0.0001336 \quad \text{volt/degree.}$$

The electromotive forces of the cell B can be expressed by the equation:

$$E = 0.52415 + 0.0002427(t-25) + 0.0000027(t-25)^2$$

and the calculated values are given in the third column of Table 2. From the above equation we obtain,

$$\left(\frac{dE}{dT}\right)_{B,298}=0.0002427 \text{ volt/degree.}$$

Substituting these numerical values for $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$ in the formula 1, we can calculate the fictitious heat of solution of zinc iodide, thus

$$(Q)_{298}=298.1(0.0001336-0.0002427)46148=-1500 \text{ cal./mol.}$$

II. The Heat of Formation of Zinc Iodide. The heat of formation of zinc iodide can be determined by applying Gibbs-Helmholtz's equation to the Cell A, in combination with the heat of formation of mercurous iodide. If the figure 14200 cal. (Nernst,⁽¹⁾ Bernoulli⁽²⁾) be taken as the heat of formation of mercurous iodide (HgI), the heat of formation of zinc iodide will be :

$$2\text{Hg}+\text{I}_2=\text{Hg}_2\text{I}_2\ ;\ \Delta H_{298}=-28400 \text{ cal.}$$

$$\text{Zn}+\text{Hg}_2\text{I}_2=\text{ZnI}_2+2\text{Hg}\ ;\ \Delta H_{298}=-22360 \text{ cal.}$$

The heat change in drawing an atom of zinc out of the amalgam being null, hence

$$\text{Zn}+\text{I}_2=\text{ZnI}_2\ ;\ \Delta H_{298}=-50760 \text{ cal.}$$

This value is found to be a little larger than that obtained by T. J. Webb⁽³⁾ as the result of his study on the cell : Ag | AgI, ZnI_2 | Zn amalgam.

III. The Free Energy of Formation and the Entropy of Mercurous Iodide. E. Cohen and his co-workers⁽⁴⁾ expressed the electromotive force of the cell : Cd amalgam | CdI_2, Hg_2I_2 | Hg as follows

$$E_1=0.41886+0.0003642\ (t-30)-0.0000003\ (t-30)^2.$$

Hence

$$\left(\frac{dE_1}{dT}\right)_{298}=0.0003672 \text{ volt/degree.}$$

The temperature coefficient of the cell : Cd | solution | Cd amalgam has been given by the expression⁽⁵⁾

$$\left(\frac{dE_2}{dT}\right)_{298}=-0.000244 \text{ volt/degree.}$$

Then the entropy change ΔS_{298} corresponding to the reaction : $\text{Hg}_2\text{I}_2+\text{Cd}=\text{CdI}_2+2\text{Hg}$ may be calculated thus :

$$\Delta S_{298}=2F\left\{\left(\frac{dE_1}{dT}\right)_{298}+\left(\frac{dE_2}{dT}\right)_{298}\right\}=5.68 \text{ entropy units.}$$

from which the entropy of mercurous iodide may be evaluated, as the entro-

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(1) Nernst. *Z. physik. Chem.*, 2 (1888), 23.

(2) Bernoulli, *Helvetica Chim. Acta*, 2 (1919), 720.

(3) Webb, *J. Phys. Chem.*, 27 (1923), 448.

(4) *Z. physik. Chem.*, 94 (1920), 210.

(5) Gerke, *Chem. Rev.*, 1 (1925), 377.

pies(1) of Hg, Cd and CdI_2 are known to be $S_{Hg}=17.8$, $S_{Cd}=11.8$ and $S_{CdI_2}=38.7$,

$$S_{Hg_2I_2}=56.8 \text{ entropy units.},$$

which is quite consistent with the value $S_{Hg_2I_2}=56.76$, calculated with the aid of the formula proposed by Latimer(2) for the entropy of solid salt:

$$S_{298}=\tfrac{3}{2}\cdot R \ln A-0.94 \text{ (A being atomic weight).}$$

The entropy change and the free energy change in the formation of mercurous iodide will be:

$$2Hg+I_2=Hg_2I_2\,;\ \Delta S_{298}=-5.4 \text{ entropy units,}$$

$$(S_{I_2}=2\times 13.3)$$

$$2Hg+I_2=Hg_2I_2\,;\ \Delta F_{298}=\Delta H_{298}-T\Delta S_{298}=-26790 \text{ cal.}$$

IV. The Free Energy of Formation of Zinc Iodide. This can be calculated as follows:

$$Zn+Hg_2I_2=ZnI_2+2Hg\,;\ \Delta F_{298}=-2EF=-24195 \text{ cal.}$$

$$2Hg+I_2=Hg_2I_2\,;\ \Delta F_{298}=-26790 \text{ cal.}$$

Hence

$$Zn+I_2=ZnI_2\,;\ \Delta F_{298}=-50985 \text{ cal.}$$

This result may be compared with that obtained by the entirely different process. The electromotive force of the cell involving the reaction $Zn+2AgI=ZnI_2+2Ag$, has been given by T. J. Webb(3): $E=0.3987$.
Hence

$$Zn+2AgI=ZnI_2+2Ag\,;\ \Delta F_{298}=-2EF=-18400 \text{ cal.}$$

and $Ag+\tfrac{1}{2}I_2=AgI\,;\ \Delta S_{298}=3.4$ entropy units.(4)

$$Ag+\tfrac{1}{2}I_2=AgI\,;\ \Delta H_{298}=-15100 \text{ cal.}^{(3)}$$

$$Ag+\tfrac{1}{2}I_2=AgI\,;\ \Delta F_{298}=\Delta H-T\Delta S=-16114 \text{ cal.}$$

so that

$$Zn+I_2=ZnI_2\,;\ \Delta F_{298}=-50628 \text{ cal.}$$

The agreement is fairly satifactory.

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(1) Lewis-Randall, "Thermodynamics," 1923; Webb, *J. phys. Chem.*, **29** (1925), 816.

(2) *J. Am. Chem. Soc.*, **43** (1921), 818.

(3) *J. Phys. Chem.*, **27** (1923), 448.

(4) Lewis-Randall, loc. cit.

ON THE EFFECTS OF GASES UPON THE SURFACE TENSIONS OF SOME LIQUIDS.(1)

By Bun-ichi TAMAMUSHI.

Received June 29, 1926. Published August 28, 1926.

Introduction. Surface tension, being a property of the boundary surface of phases, should be effected by the nature of phases on both sides of the surface. According to the classical works of Quincke,(2) Kundt,(3) and Guye and Renard,(4) it is evident that air has a certain effect, though not so considerable, upon the surface tension of pure water. In later years Ferguson(5) studied the effects of air and carbon dioxide on the surface tensions of some organic liquids. The present paper contains the results of measurements made on the following pairs of gases and liquids. Gas : air, carbon dioxide, nitrous oxide, hydrogen sulphide. Liquid : water, ethyl alcohol, ethyl ether, carbon bisulphide, carbon tetrachloride.

Experimentals. The apparatus of Ramsay and Shields(6) is somewhat modified in the present research as is shown in Fig. 1, particularly for the purpose of easily saturating solvent with gas. This is done by the side tube B, which is connected to a generator of gas and also to a manometer. The top of the wide tube A is provided with a good stop cock and the whole U tube is protected, to its neck, by a water jacket of temperature constant within the fluctuation of less than ±0.1°.

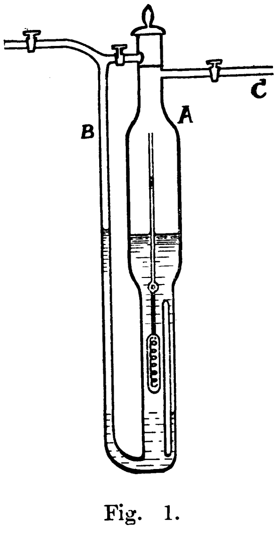

Fig. 1.

Two capillary tubes were very carefully selected and examined and their radii have been found to be 0.0142 cm. and 0.0166 cm. respectively. The rise of liquid in the capillary tube was measured by a cathetometer of Société Genevoise with an accuracy to 0.005 cm., and corrections due to the curvature of meniscus were calculated by means of Lord Rayleigh's(7) formulae.

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(1) Read before the Chemical Society of Japan, October 1924.
(2) *Pogg. Ann.*, **160** (1877), 573.
(3) *Wied. Ann.*, **12** (1881), 538.
(4) *J. chim. phys.*, **5** (1907), 81.
(5) *Phil. Mag.*, (6), **28** (1914), 403.
(6) *J. Chem. Soc.*, **63** (1893), 1089.
(7) *Proc. Roy. Soc.*, [A] **92** (1915), 184.

In the course of measurement the capillary rise of a pure solvent is at first read under its own vapour pressure (the apparatus being previously evacuated through another side tube C) and then letting the gas pass into the solvent under a certain pressure less than one atmosphere and when the equilibrium is attained the height of the capillary column is again measured, due care being taken of the constancy of temperature in the jacket during all these processes.

The surface tension is calculated by the following formula:

$$\sigma=\frac{1}{2}g\,r\,(h+h')\,(D-d)$$

where g: gravity constant, r: radius of capillary tube, h: capillary rise read by cathetometer, h': correction term, D: density of liquid determined by pyknometer in each case, d: density of gas phase, which was taken from Landolt-Börnstein's Tables and the related small corrections have been calculated by the law of ideal solution. The depression of surface tension is expressed in percentage as $100\frac{\Delta\sigma}{\sigma}$, $\Delta\sigma$ being the difference of surface tensions between solvent and solution, σ being the surface tension of pure solvent. The experimental results are shown in the following tables, in which p denotes the pure solvent and s solution.

TABLE 1. Air.

Solvent	Temp.	$100\frac{\Delta\sigma}{\sigma}$
Water	20	0.22
Ethyl alcohol	19	0.46
Benzene	18	0.32
Ethyl ether	20	0.40

TABLE 2. Carbon dioxide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	18.0	p	8.694	0.9986	70.95	0.83
		s	8.631	0.9974	70.36	
CCl_4	25.0	p	1.9633	1.5822	25.27	0.96
		s	1.9453	1.5815	25.03	
CS_2	24.8	p	2.960	1.2620	30.39	0.95
		s	2.935	1.2607	30.10	
$(C_2H_5)_2O$	25.3	p	2.759	0.7067	15.82	0.97
		s	2.721	0.7078	15.67	
C_2H_5OH	25.3	p	3.317	0.7860	21.21	0.99
		s	3.287	0.7854	21.00	
C_6H_6	25.1	p	3.803	0.8714	26.96	0.96
		s	3.771	0.8705	26.70	

TABLE 3. Nitrous oxide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	25.2	p	8.685	0.9968	70.43	0.75
		s	8.635	0.9951	69.90	
C_2H_5OH	25.1	p	3.319	0.7870	21.25	0.97
		s	3.292	0.7858	21.04	
$(C_2H_5)_2O$	25.0	p	2.774	0.7067	15.95	0.82
		s	2.750	0.7071	15.82	
CCl_4	24.8	p	1.962	1.5822	25.26	0.96
		s	1.943	1.5823	25.01	

TABLE 4. Hydrogen sulphide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	15.2	p	8.740	0.9990	71.36	1.19
		s	8.640	0.9985	70.51	
C_2H_5OH	16.1	p	3.388	0.7948	22.15	1.26
		s	3.340	0.7960	21.87	
C_6H_6	15.3	p	3.954	0.8829	28.67	1.22
		s	3.900	0.8843	28.32	

TABLE 5.

Solvent	Gas	Concentration C	$C^{\frac{1}{3}}$	$100\frac{\Delta\sigma}{\sigma}$
Water	Air	0.00236	0.133	0.22
	N_2O	0.104	0.470	0.75
	CO_2	0.145	0.525	0.83
	H_2S	0.334	0.694	1.19
C_2H_5OH	Air	0.0232	0.285	0.46
	N_2O	0.647	0.865	0.97
	CO_2	0.693	0.885	0.99
	H_2S	1.870	1.232	1.26
C_6H_6	Air	0.0205	0.274	0.32
	CO_2	0.571	0.830	0.96
	H_2S	1.084	1.027	1.22

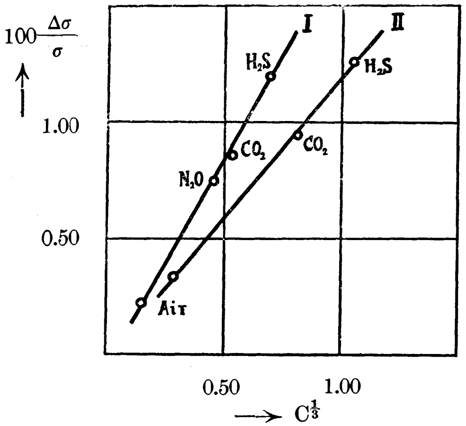

Fig. 2. I: Water.
II: Benzene.

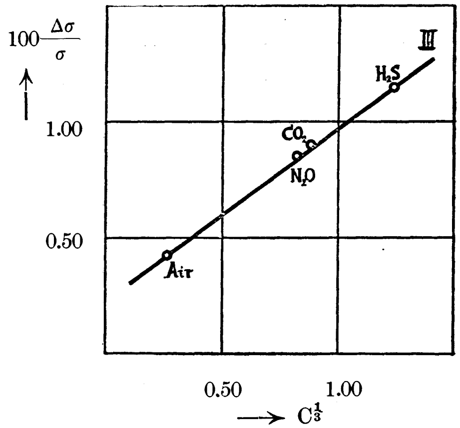

Fig. 3. III: Alcohol.

Discussions. The depressive effects of air upon these liquids are in the mean not greater than five percent; values of the same order were obtained also by the other authors already mentioned.

If we compare the values of $\frac{\Delta\sigma}{\sigma}$ with each other for a given gas and different liquids, it is remarkable that they are almost constant in each series, that is, the greater the surface tension the greater the effect of depression. It must be mentioned that similar facts were observed by Ferguson in his experiments above refered. The rule of this kind is certainly not insignificant, however its theoretical explanation may not be simple as the complex nature of adsorption and of other related phenomena must be taken in consideration.

Table 5 shows the relation between the values of $\frac{\Delta\sigma}{\sigma}$ and the concentrations of different gases dissolved in the same solvent. The values of solubilities are quoted from Seidell's Tables except one, i.e. the solubility of hydrogen sulphide in bengene, which has been determined by the author, the details of the method being here omitted. As it is shown in this table or in Fig. 2 and 3, the relation between the cube root of concentration and $\frac{\Delta\sigma}{\sigma}$ is nearly linear in each case, that is, for a system of same liquid and different gases we have an empirical relation as follows:

$$\frac{\Delta\sigma}{\sigma}=kC^{\frac{1}{3}}+a$$

where k and a are certain constants. In other words, as a is in general very small, $\frac{\Delta\sigma}{\sigma}$ is almost proportional to the linear distances of molecules of the adsorbate. It may be also remarked that this formula has in its form a certain analogy with the adsorption isotherm of Freundlich.

The author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance during this work.

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Hongo, Tokyo.

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. II. THE ACTION ON OXIMES.

By **Harushige INOUE.**

Received May 17, 1926. Published August 28, 1926.

Mailhe and Godon(1) have noticed that aldoximes and ketoximes were transformed into nitriles by the catalytic action of alumina at high temperature. The action of Japanese acid earth on oximes, therefore, was studied by the present writer from the view point of contact action, and the following interesting results were obtained.

1. **Acetophenone oxime.** 20 grams of acetophenone oxime (m.p. 58–59°) mixed with 10 grams of Japanese acid earth in a flask, were heated gradually on an oil-bath. When the temperature of the bath reached 180°, a violent reaction suddenly took place as we sometimes meet in case of Beckmann's rearrangement of oximes, and whereas some volatile liquid distilled out through the side tube of the flask, a solid reaction product remained in it. Both the liquid and solid reaction products were treated separately with ether and then hot water; the ethereal solution was treated with ammonia and dilute hydrochloric scid successively to get off the acidic and basic substances from a neutral substance which is formed simultaneously by the reaction. Acetic and benzoic acids from the acidic fraction, and ammonia and aniline from the basic one were isolated and confirmed to be so by their chemical properties. Benzonitrile was isolated from the neutral reaction product, which was confirmed, by saponification with alcoholic potash, by transforming into benzoic acid (m.p. 121°) and ammonia. Acetophenone was also noticed to occur with the nitrile in the neutral reaction product in isolating in a pure state. From the hot aqueous solution, acetanilide (m.p. 115°, N=10.32%) was obtained in a pure state. The yield of the reaction products is shown in Table 1.

2. **Benzophenone oxime.** When benzophenone oxime (m.p. 139°) was treated in the same manner as the acetophenone oxime, the rearrangement

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(1) Mailhe and Godon, *Bull. Soc. Chim.*, (4), **23** (1918), 18.

was noticed to take place at 145° and benzanilide (m.p. 160°), benzonitrile, benzoic acid and other substances of unknown chemical nature were actually obtained from the reaction product, and the quantity of these substances is shown in Table 1.

3. **Menthone oxime.** Menthone oxime (m.p. 53–55°), when treated with the catalyst at 200°, was transformed into decylenic acid, methonitrile, menthone and a hydrocarbon, and the yield of these substances is shown in Table 1.

TABLE 1.

Oximes	Sample used gr.	Acid gr.	Base gr.	Acid amide gr.	Nitrile gr.	Neutral subst. gr.	NH_3
Acetophenone oxime	20.0	0.69	0.81	1.33	0.55	4.20	+
Benzophenone oxime	12.5	0.12	0.63	2.04	0.04	4.81	+
Menthone oxime	12.9	0.46	0.60	—	0.55	5.81	+

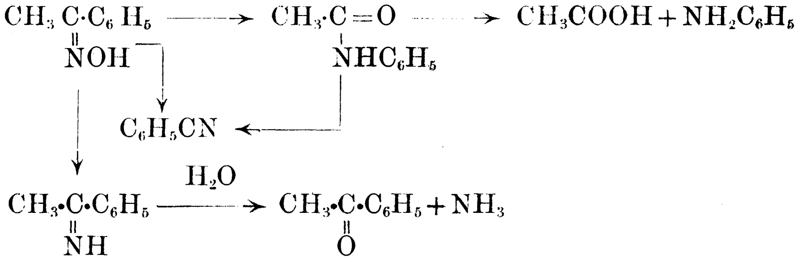
As a matter of fact, acids, nitriles, acid amides and bases were formed from oximes by contact action of Japanese acid earth, and the nitriles were naturally regarded as forming directly from the oximes as in the case of the catalytic action of alumina and also indirectly from acid amides or isoximes which resulted from the oximes by the Beckmann rearrangement. In the present case, the writer was inclined to believe that the Beckmann rearrangement was one of the principal reactions of oximes caused by the contact action of Japanese acid earth at about 150–200°, since acetanilide and benzanilide were actually isolated with a large yield from the reaction products of acetophenone and benzophenone oximes respectively, and aniline which occurs in the reaction product in both cases, was explained to be formed by hydrolysis of the anilides. In order to confirm the above assumption for the transformation of anilides into aniline, acid and nitrile, by the contact action of the earth, 10 grams of acetanilide and of benzanilide were passed respectively on the catalyst heated at 300°, aniline, acids and nitrile were confirmed to occur in the reaction products as will be seen in the following table.

TABLE 2.

Acid amides	Acid amide unchanged gr.	Nitrile	Base (aniline) gr.	Acid gr.	NH_3
Acetanilide	0.55	a little	1.87	0.014	+
Benzanilide	0.55	a little	0.37	0.012	+

When, however, 20 grams of benzonitrile (b. p. 183—184°; density= 1,0068) were passed on the same catalyst heated at 250°, no appreciable reaction was noticed to take place.

Thus, the transformation of ketoximes by the contact action of Japanese acid earth, into their isomeric acid amides, nitriles, acids, amines and ketones was represented with an example of acetophenone oxime, by the following scheme:



The formation of acetophenone from its oxime was explained by the direct hydrolysis of the oxime on the one side, and on the other by assuming the formation of methyl phenyl-ketimine as an intermediate, as indicated by Lachman.(1)

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(1) Lachman, *J. Am. Chem. Soc.*, **46** (1924), 1477.

STUDIES ON MERCAPTALS OF SUGARS. I. NORMAL BUTYL MERCAPTALS OF SUGARS.(2)

By Yoshisuke UYEDA and Jinzō KAMON.

Received July 19, 1926. Published August 28, 1926.

Fisher(3) found that a glucoside was produced by the condensation of the sugar and the alcohol in presence of hydrochloric acid. When the aldehyde being treated with the mercaptan, a substance " mercaptal," named by Baumann,(4) was prepared. Fisher(5) obtained various mercaptals in crystalline

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(2) Read before the Chemical Society of Japan, April 6, 1924. The original paper will be published in the *Journal of the Chemical Society of Japan*, and this is an abstract from the original one.

(3) Fisher, *Ber.*, 26 (1893), 2400.

(4) Baumann, *Ber.*, 18 (1885), 884.

(5) Fisher, *Ber.*, 27 (1894), 673.

form by the condensation of sugars and mercaptans in presence of concentrated hydrochloric acid. He used ethyl and amyl mercaptan.

The present authors have studied on the normal butyl mercaptals of various sugars and obtained various crystalline mercaptals. Five monoses, arabinose, glucose, galactose, mannose and rhamnose; three dioses, lactose, maltose and sucrose were tried and the mercaptals thus prepared were crystallized from dilute alcohol. Xylose and fructose were tried, but ended in negative results.

The new mercaptals of sugars prepared by us have the following formula, which were ascertained by the analysis.

Glucose-N-butyl mercaptal		$C_6H_{12}O_5(C_4H_9S)_2$
Galactose	,,	$C_6H_{12}O_5(C_4H_9S)_2$
Mannose	,,	$C_6H_{12}O_5(C_4H_9S)_2$
Rhamnose	,,	$CH_3\ C_5H_9O_4(C_4H_9S)_2$
Arabinose	,,	$C_5H_{10}O_4(C_4H_9S)_2$
Maltose	,,	$C_{12}H_{22}O_9(C_4H_9S)_4$
Lactose	,,	$C_{12}H_{22}O_9(C_4H_9S)_4$
Sucrose	,,	$C_{12}H_{22}O_9(C_4H_9S)_4$

The physical constants of these mercaptals have been measured and are tabulated as follows.

		M.p.	Sp. rotation.
Glucose-N-butyl mercaptal		124°	$[\alpha]_D^{12°} = +27.00$
Galactose	,,	123	,, $= +12.67$
Mannose	,,	117	$[\alpha]_D^{8°} = +16.45$
Rhamnose	,,	119	,, $= +16.49$
Arabinose	,,	111.5	,, $= +14.00$
Maltose	,,	126	,, $= +12.00$
Lactose	,,	106	,, $= +23.55$
Sucrose	,,	123	,, $= +\ 3.71$

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STUDIES ON MERCAPTALS OF SUGARS. II. NORMAL PROPYL MERCAPTALS OF SUGARS.

By Yūichi MAEDA and Yoshisuke UYEDA.

Received July 5, 1926. Published August 28, 1926.

Normal butyl mercaptals of sugars have been studied by one of the authors (Uyeda) and Kamon, and are described in the previous paper. Now, the authors have tried to study on the normal propyl mercaptals of sugars, according to Fisher's method. The outline of the results is reported in this paper.

Experimental. Mercaptals are prepared by the following method: Each sugar is dissolved in equal quantity of concentrated hydrochloric acid (sp. gr. 1.20), to whose solution, a little excess of molecular proportion of normal propyl mercaptan being added, well shaken and stand over night. Most of them begin to crystallize out within an hour. The crystalline product is filtered, washed with water, and dried on the porous tile. The crude products thus obtained are purified by the recrystallization from dilute alcohol, the mercâptals are nice white crystalline needles.

The physical constants and the results of analysis are summarized in the following tables:

TABLE 1. Properties of Mercaptals.

	M.p.	Sp. rotation $[\alpha]_D^{17°}$
Glucose N-propyl mercaptal	147°	+41°
Galactose ,,	129	+27.5
Mannose ,,	125	+31
Rhamnose ,,	130	+10
Arabinose ,,	128	+29
Maltose ,,	146	+25
Sucrose ,,	146	+13.5

TABLE 2. Analysis of Mercaptals.

		Sulphur	
		Calc. %	Found %
Glucose N-propyl mercaptal	$C_6H_{12}O_5(C_3H_7S)_2$	20.38	20.07
Galactose ,,	$C_6H_{12}O_5(C_3H_7S)_2$	20.38	20.15
Mannose ,,	$C_6H_{12}O_5(C_3H_7S)_2$	20.38	20.01
Rhamnose ,,	$CH_3\ C_5H_9O_4(C_3H_7S)_2$	21.47	21.24
Arabinose ,,	$C_5H_{10}O_4(C_3H_7S)_2$	22.53	22.20
Maltose ,,	$C_{12}H_{22}O_9(C_3H_7S)_4$	20.98	20.61
Sucrose ,;	$C_{12}H_{22}O_9(C_3H_7S)_4$	20.98	20.68

The sulphur was determined by using sodium peroxide in Parr bomb.

Other sugars than these, namely xylose, fructose and lactose, were tried, but ended in negative results.

Summary.

The following sugars were obtained as new crystalline mercaptals by treatments with normal propyl mercaptan :—

Three hexoses, glucose, galactose and mannose ; one pentose, arabinose, one methyl pentose, rhamnose ; two dioses, maltose and sucrose.

Our sincere thanks are due to Assistant Professor Ishinada, who kindly checked carefuly the physical constants of our samples.

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FREEZING CURVES OF THE SYSTEMS BENZENE-ETHER AND BENZENE-ACETONE.

By Shiro YAMAMURA.

Received July 12, 1926. Published September 28, 1926.

The System Benzene-Ether. The melting points of the mixtures of benzene and ethyl ether was studied by Pickering.(1) But his results is not complete one and want the part of 80–100 percent ether.

My apparatus for the measurement of the freezing point of the mixture was very similar to that usually used in the determination of the freezing point depression of dilute solutions. Special precautions, however, were taken to prevent the introduction of water vapour into the liquid mixture. 10–15 c.c. of liquid mixture was introduced into a glass tube in which a pentane thermometer and a stirrer were inserted. The tube was cooled from outside with cooling agent such as solid carbon dioxide or liquid air. To regulate the rate of cooling of the liquid, the tube was protected with a partially evacuated Dewar vessel which then dipped into the cooling agent. A pentane thermometer having the certificate of the " Physikalisch-Technische Reichsanstalt " was used for the measurement of low temperature. This kind of thermometer however, cannot be used to measure the temperature in greater accuracy than half a degree. Moreover the correction of reading for the exposed thread of pentane amounted to a few degrees in some cases, so this must be taken into consideration in the determination of freezing point.

The results of the measurement were as follows.

Mol % of ether.	Freezing point.	Mol % of ether.	Freezing point.
0 (pure C_6H_6)	+ 5°.1	74.5	− 61°.3
5.1	+ 1.7	80.3	− 71.7
7.0	+ 0.4	82.0	− 74.5
14.9	− 4.3	82.3	− 79.
16.0	− 4.8	85.1	− 88.5
25.1	− 11.2	87.7	− 94.
30.6	− 14.9	90.4	−105.
35.1	− 18.6	91.3	−106.
39.5	− 22.6	92.4	−115.5
44.9	− 27.0	92.7	−118.5
49.6	− 33.0	94.8	−126.5
55.0	− 36.9	94.9	−126.5
59.6	− 43.4	97.1	−125.
64.1	− 48.0	97.6	−124.5
69.7	− 52.5	100. (pure $C_4H_{10}O$)	−123.5 (meta-stable form)

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(1) Pickering, *J. Chem. Soc.*, **63** (1893), 998.

Graphically it becomes as Fig. 1.

The System Benzene-Acetone. The method of measurement is quite the same as the system mentioned above. The results were as follows.

Mol % of acetone.	Freezing point.	Mol % of acetone.	Freezing point.
0 (pure C_6H_6)	+ 5.1°	81.8	– 61.°
21.3	– 5.	84.2	– 68.
33.4	– 15.	86.0	– 72.
46.7	– 22.	89.1	– 83.
52.0	– 25.	89.9	– 87.
59.5	– 32.	96.6	– 96.0
69.1	– 40.	100. (pure C_3H_6O)	– 94.8

It is shown graphically in Fig. 2.

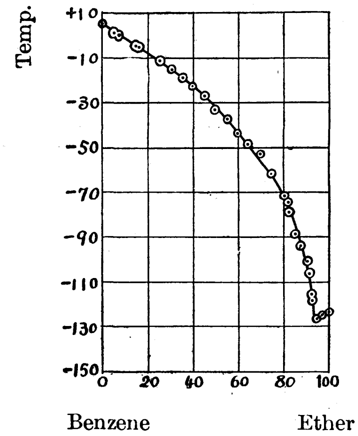

Fig. 1.

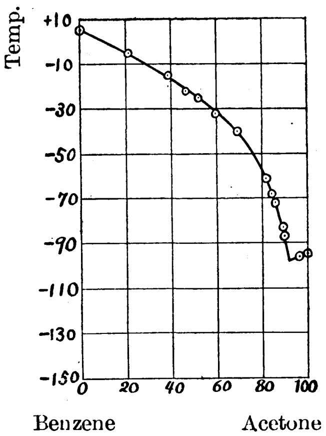

Fig. 2.

The author's thanks are due to Prof. J. Sameshima for his kind guidance.

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ON THE DERIVATION OF ADSORPTION ISOTHERMS.

By **Bun-ichi TAMAMUSHI.**

Received July 26, 1926. Published September 28, 1926.

With regard to a surface containing adsorbed substance Volmer(1) assumed the following characteristic equation,

$$(\gamma_0-\gamma)\left(\frac{1}{u}-\beta\right)=RT \cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

in which γ_0 is the surface tension of pure solvent, γ that of solution, u the excess of solute in unit surface, so that according to Volmer's notation $\frac{1}{u}=\Omega$ being the area of the surface where one mol of the solute is adsorbed, β the actual area occupied by the molecules of solute per mol in the surface, R the gas constant, and T the absolute temperature.

Kar(2) has given this equation a theoretical foundation by the method of statistical mechanics and also from this equation he has derived the adsorption isotherm of Langmuir(3) which is expressed as follows :

$$C=\frac{ku}{1-aNu} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where C is the concentration of solute in the interior of solution, u the excess of solute in the surface, a the area of a molecule of solute, and N Avogadro's number. Therefore aN is equal to β in equation (1).

To derive the equation of Langmuir from that of Volmer, another equation which involves γ, C and u will be necessary. The following form fits for the purpose :

$$\frac{u}{1-u\beta}=-\frac{C}{RT}\frac{d\gamma}{dC} \cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

This may, namely, be called a revised equation of Gibbs since a due correction being made on the left side of the original equation.

Now differentiating equation (1) at constant temperature,

$$-d\gamma=\frac{RT}{(1-u\beta)^2}du$$

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(1) *Z. physik. Chem.*, 115 (1925), 253.
It may be remarked that the equation of Volmer represent a particular case of Gibbs' equation when the solution is so dilute as we can put $C \doteq dC$ and $\gamma_0-\gamma=-d\gamma$ in the latter equation.

(2) *Physik. Z.*, 26 (1925), 615.

(3) *J. Am. Chem. Soc.*, 40 (1918), 1361.

and from equation (3) we get

$$-d\gamma = RT\frac{u}{1-u\beta}\frac{dC}{C}.$$

Equating these relations,

$$\frac{RT}{(1-u\beta)^2} = RT\frac{u}{1-u\beta}\frac{dC}{C}.$$

Hence we have

$$\frac{dC}{C} = \frac{du}{u(1-u\beta)}.$$

By integration

$$\int\frac{dC}{C} = \int\left(\frac{1}{u}+\frac{\beta}{1-u\beta}\right)du + \text{const.}$$

so that we have

$$\ln C = \ln u - \ln(1-u\beta) + k$$

where k is a constant of integration.
Thus it becomes

$$C = \frac{ku}{1-u\beta}$$

or

$$C = \frac{ku}{1-aNu}.$$

This is the adsorption isotherm of Langmuir which was obtained in his theory of monomolecular film and also experimentally confirmed by him.

Now the Gibbs' equation in its original form will be used instead of the equation (3) and γ will be eliminated in the following manner.

$$u = -\frac{C}{RT}\frac{d\gamma}{dC} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

or

$$-d\gamma = \frac{dC}{C}uRT,$$

equating this and the differential of equation (1), we have

$$\frac{dC}{C} = \frac{du}{u(1-u\beta)^2}.$$

By integration

$$\int\frac{dC}{C} = \int\frac{du}{u(1-u\beta)^2} + \text{const.}$$

i.e.

$$\int \frac{dC}{C} = \int \left(\frac{1}{u} + \frac{\beta}{1-u\beta} + \frac{\beta}{(1-u\beta)^2} \right) du + \text{const.}$$

therefore it becomes

$$\ln C = \ln u - \ln (1-u\beta) + \frac{1}{1-u\beta} + \lambda$$

in which λ is an integration constant.
Hence we obtain

$$C = \frac{u}{1-u\beta} e^{\lambda + \frac{1}{1-u\beta}}$$

or

$$C = \lambda' \frac{u}{1-u\beta} e^{\frac{u\beta}{1-u\beta}} \quad \cdots\cdots\cdots\cdots \cdots\cdots\cdots (5)$$

where λ' denotes a certain constant.

This formula is analogous to that of Schmidt⁽¹⁾ as will easily be shown in the following transformation.

Since we can put $u = \omega x$, x being the total amount of adsorption, and $\frac{1}{\omega}$ the area of adsorption surface, equation (5) is transformed into

$$C = \lambda' \frac{\omega}{1-\omega\beta x} x\, e^{\frac{\omega\beta x}{1-\omega\beta x}}$$

or

$$C = \lambda' \omega e^{\omega\beta S} \frac{x}{1-\omega\beta x} e^{\omega\beta \left(\frac{x}{1-\omega\beta x} - S \right)}$$

Here S denotes the maximum amount of adsorption. Moreover put

$$\lambda' \omega e^{\omega\beta S} = \frac{K}{S}, \qquad \omega\beta = -A,$$

then we have

$$C = \frac{K}{S} \frac{x}{1-\omega\beta x} e^{A\left(S - \frac{x}{1-\omega\beta x} \right)}$$

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(1) *Z. physik. Chem.*, **77** (1911), 645 ; **88** (1913), 677.

Comparing this equation with that of Schmidt i.e.,

$$C=\frac{K}{S}xe^{A(S-x)}$$

we see that the former is identical with the latter provided that x being corrected by $(1-u\beta)$.

The effect of the correction term $(1-u\beta)$ in these equations in consideration may not be so great, but it affects in such sense as to make the value of u greater, since $(1-u\beta)<1$. This relation seems to afford an explanation for the deviation seen in the experimental verifications of the equation of Gibbs. In the works of this kind the calculated value of u tends mostly to be smaller than that of the observed one, as was the case in the work of Mc Lewis(1) or of Donnan and Barker.(2) The fact, however, is not simple for other possible corrections which would affect the balance of energy might also be taken into account.

Now if the equation of Volmer is simplified by dropping the correction β, we have

$$(\gamma_0-\gamma)\frac{1}{u}=RT \quad \cdots\cdots\cdots\cdots(1')$$

Moreover, if a correction analogous to van't Hoff's coefficient be introduced into this equation we have

$$(\gamma_0-\gamma)\frac{1}{u}=iRT \quad \cdots\cdots\cdots\cdots(1'')$$

in which i is a certain correction factor. Combining either one of these equations with equation (4) and (3) respectively so as to eliminate γ in the similar way as before, there are obtained several adsorption isotherms.

From equations (1′) and (4), $C=ku$ that is, Henry's law follows as the simplest case, and from (1′) and (3) we get $C=ue^{-\beta u+\text{const.}}$ i.e. a formula of Schmidt's type. Similarly from (1″) and (4) we obtain $C=ku^i$ i.e. a formula which is identical with that of Freundlich, and from (1″) and (3) $C=u^ie^{-i\beta u+\text{const.}}$, a formula which is of Freundlich's type and expresses also the state of saturation.

Further studies on this subject will be done.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance.

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(1) *Phil. Mag.*, (6), 15 (1908), 499.
(2) *Proc. Roy. Soc.*, A, 85 (1911), 557.

A RELATION BETWEEN ORTHOBARIC DENSITIES.

By Jurô HORIUCHI.

Received August 9, 1926. Published September 28, 1926.

The distribution of infinitesimal molecules in phases having different potential energies is expressed in the following classical equation,

$$\frac{N_1}{N_2}=e^{\frac{-(\psi_1-\psi_2)}{RT,}} \qquad \text{or} \qquad -(\psi_1-\psi'_2)=RT\ln\frac{N_1}{N_2}\,,$$

where N_1 and N_2 denote the molecular density in the phase of the potential energy ψ_1 and ψ_2 respectively. Now to discuss the orthobaric state of coexistent liquid and vapour, the molecule cannot be regarded as of infinitesimal size. Consequently we can introduce a proper correction to either side of the above equation. In the following discussion, it is supposed that due correction has been introduced in ψ, so that $\psi_1-\psi_2$ does not express the actual internal heat of evaporation, but the increase of potential energy when the molecule of infinitesimal size be transfered from liquid to the gaseous phase. The foregoing equation can be modified in the following form,

$$-(\psi_1-\psi_2)=\psi=RT\ln\frac{D_l}{D_g}=RT\ln\frac{V_g}{V_l}, \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where V_l, D_l, V_g and D_g represent the molecular volume and the density of liquid and those of vapour respectively. Under the assumption that the internal pressure should be proportional to the square of the density, van der Waals and his followers gave an expression a/v^2 for the internal pressure. Integrating this, we obtain the following relation for the potential difference between two states having the molecular volume V_g and V_l,

$$\psi=\int_{V_l}^{V_g}\frac{a}{V^2}dV=a\left(\frac{1}{V_l}-\frac{1}{V_g}\right)=RT\ln\frac{V_g}{V_l}\,.$$

It is well known that this does not agree with experiments. However subtracting a certain quantity E, characteristic to individual substances, the resulting equation was found to be concordant with actual measurements i.e.

$$\psi=RT\ln\frac{V_g}{V_l}=A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)\cdots\cdots\cdots\cdots\cdots(2)$$

where A is a constant characteristic to each substance. This expression may be regarded as a proper form to express virtual internal heat of vaporization for infinitesimal molecules. In the literatures there are found equations analogous to (2). Goebel⁽¹⁾ derived a equation of state for gases, giving an expression $\frac{a}{(V-a)^2}$ for the internal pressure. The region of validity of his equation was found to be $t>t_k$, $p>p_k$, and $V>1.9b$, and it failed at the temperature and pressure below that of the critical point.

Keyes,⁽²⁾ adopting the form $\frac{A}{(V+l)^2}$ for the internal pressure, has shown that the value of l is negative for hydrogen and air, while it is positive for mathane and others.

Now, the calculation of the present author ranges from the critical temperature to those below the room temperature and shows good agreement with the experimental data. Goebel's equation has the purpose to express actual internal pressure, while that of the present author intends to express a relation between orthobaric densities. Consequently these two equations, though resembling in their form, are essentially different, and the numerical values of constants being of course quite different.

If we assume that the internal heat of vaporization L_i can be obtained by integrating Goebel's expression, then we have

$$L_i=\int_{V_l}^{V_g}\frac{a}{(V-a)^2}\,dV=\frac{a}{V_l-a}-\frac{a}{V_g-a}\quad\cdots\cdots\cdots\cdots\cdots(3)$$

Combining (3) with Dieterici's empirical equation,⁽³⁾ $L=CRT\ln V_g/V_l$, where C is close to 1.7, we obtain a relation

$$CRT\ln\frac{V_g}{V_l}=\frac{a}{V_l-a}-\frac{a}{V_g-a}\quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

Thus equation (2) is formally equivalent to the Goebel's equation, extended to orthobaric states and combined with Dieterici's rule. In equation (2), however, the actual value of L_i is not taken in consideration, but it simply expresses a relation between orthobaric densities, and agrees excellently with experimental data as is shown in the following tables.

The calculation has been undertaken for the following 21 substances, which are possibly different in chemical nature : hydrogen, oxygen, nitrogen, argon, carbon dioxide, i-pentane, n-octane, benzene, hexamethylene, chlorobenzene, carbon tetrachloride, stannic chloride, methyl acetate, ethyl formate, propyl formate, methyl butylate, ethyl ether, methyl alcohol, ethyl alcohol,

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(1) *Z. phys. Chem.*, 47 (1904), 471; 49 (1905), 129; 50 (1905), 238.

(2) *Proc. Nat. Acad. Sci.*, 3 (1917), 323.
J. Am. Soc. Refrig. Eng., 1 (1914), 9; 7 (1921), 371.
J. Am. Chem. Soc., 41 (1919), 589; 42 (1920), 54; 43 (1921), 1452.
J. Math. Phys. Mass. Inst. Tech., 1 (1922), 89, 191, 211 & 243.

(3) *Ann. Phys.*, 25 (1908), 569.

propyl alcohol and acetic acid. In this paper, however, abridged data⁽¹⁾ for only 8 substances are shown to save the space. Also the value expressed by the equation $q=RT \ln V+A/(V-E)$, has been calculated for liquid and vapour respectively, and they are given in the table as q_l and q_g. In the calculation the value of R is taken as 1.988 calories.

TABLE 1. Hydrogen.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
− 258°.27	0.07631	0.00020	175.1	178.0	278.3	275.4
− 253.76	0.07192	0.00101	163.9	164.3	294.4	294.0
− 247.79	0.06116	0.00405	138.6	137.6	319.2	320.2
− 245.73	0.06050	0.00613	124.2	124.1	327.4	327.5
− 240.57	0.04316	0.01922	52.2	54.0	341.5	339.7
		$A=3958$		$E=4.20$.		

(H. K. Onnes, Crommelin and Cath, *Verhl. Akad. Wet. Amst.*, 26 (1917), 192.)
(Mathias, Crommelin and Onnes, *Compt. rend.*, 172 (1921), 262.)

TABLE 2. Oxygen.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
− 210°.4	1.2746	0.0001	1.2×10^3	1175	1577	1.6×10^3
− 182.0	1.1415	0.0051	979	988	1594	1585
− 154.5	0.9758	0.0385	761	763	1606	1604
− 129.9	0.7781	0.1320	504	499	1634	1639
− 120.4	0.6032	0.2701	243	251	1622	1614
		$A=18160$		$E=9.68$		

(Mathias and Onnes, *Comm. Phys. Lab. Leiden*, No. 117 (1917).)

TABLE 3. Isopentane.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.6393	0.0011	3459	3457	6026	(6028)
40	0.5988	0.004456	3051	3054	6047	6044
70	0.5656	0.01013	2742	2742	6075	6075
100	0.5278	0.02020	2420	2431	6133	6122
130	0.4826	0.03831	2032	2026	6146	6152
160	0.4206	0.07289	1511	1515	6161	6157
180	0.3498	0.1258	923	946	6138	6115
187.4	0.2761	0.1951	319	337	6079	6031
		A=204300		$E=53.8$.		

(Young, *Sci. Proc. Roy. Dublin Soc.*, 12 (1910), 374)

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(1) Full data will be published in the *Journal of the Chemical Society of Japan*.

TABLE 4. Chlorobenzene.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
80°	1.0419	0.0008	5035	5062	8349	8322
100	1.0193	0.0014	4886	4863	8354	8377
120	0.9960	0.0026	4650	4657	8357	8350
140	0.9723	0.004316	4449	4452	8363	8360
160	0.9480	0.006784	4253	4254	8384	8383
180	0.9224	0.01023	4054	4054	8407	8407
200	0.8955	0.01506	3841	3841	8425	8425
220	0.8672	0.02145	3625	3623	8450	8452
240	0.8356	0.03000	3393	3385	8464	8472
260	0.8016	0.04172	3132	3131	8483	8484

$A=292700$ $E=50.15$

(Young, ibid.)

TABLE 5. Carbon tetrachloride.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
30°	1.5748	0.0012	4326	4339	7101	7088
60	1.5165	0.0033	4059	4054	7116	7121
90	1.4554	0.007955	3760	3762	7138	7136
120	1.3902	0.01639	3471	3470	7172	7173
150	1.3215	0.03040	3172	3173	7221	7220
180	1.2470	0.05249	2855	2851	7271	7265
210	1.1566	0.08787	2475	2479	7313	7309
240	1.0444	0.1464	2004	2023	7342	7323
270	0.8666	0.2710	1256	1326	7327	7257

$A=232000$ $E=44.3$

(Young, ibid.)

TABLE 6. Methyl acetate.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_{ε}
0°	0.95932	0.0003	4400	4405	6765	(6760)
50	0.8939	0.002212	3855	3847	6688	6696
110	0.8060	0.01239	3181	3178	6651	6654
170	0.6907	0.04598	2388	2393	6621	6616
230	0.5427	0.2028	803	850	6479	6432

$A=173700$ $E=37.8$

(Young, ibid.)

TABLE 7. Ethyl ether.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
−101.3°	0.8435	0.40×10^{-6}(M.)	4976	4999	6526	6503
− 81.0	0.8227	3.61×10^{-6}(M.)	4711	4713	6433	6431
− 64.4	0.8056	15.74×10^{-6}(D.)	4499	4498	6374	6375
− 35.0	0.7749	12.59×10^{-5}(T.)	4129	4132	6291	6288
+ 20	0.7135	18.70×10^{-4}(Y.)	3467	3488	6197	6176
+ 60	0.6658	67.71×10^{-4}(Y.)	3039	3042	6179	6176
+ 90	0.6250	0.01477 (Y.)	2698	2699	6188	6187
+140	0.5385	0.04488 (Y.)	2040	2022	6181	6199
+190	0.3663	0.1620 (Y.)	749	769	6114	6094
		$A=185600$		$E=50.0$		

T : Taylor and Smith, *J. Am. Chem. Soc.*, **44** (1922), 2450.
D : Drucker and Kangro, *Z. physik, Chem.*, **90** (1915), 518.
M : Mündel, *Z. physik. Chem.*, **85** (1913), 456.
Y : Young, ibid.

Vapour densities with indices T, D and M have been calculated from vapour tensions given by these authors applying the ideal gas low, and those of liquid at low temperatures have been obtained by interpolation from above mentioned Taylor and Smith's results.

TABLE 8. Methyl alcohol.

Temp. C.	D_l	D_g	$RT\ln V_g/V_l$	$A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$	q_l	q_g
0°	0.8100	0.0000562	5195	5217	7214	7192
40	0.7740	0.0004394	4650	4652	6970	6968
80	0.7355	0.002084	4117	4120	6775	6772
120	0.6900	0.007142	3569	3569	6586	6586
160	0.6340	0.01994	2978	2973	6400	6405
200	0.5530	0.05075	2247	2225	6171	6193
230	0.4410	0.1187	1312	1315	5923	5920
237	0.3850	0.1607	886	890	5825	5821
239	0.3504	0.1878	645	638	5774	5771
		$A=78950$		$E=24.40.$		

(Young, ibid.)

These tables show that the deviation between two quantities $RT\ln V_g/V_l$ and $A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$ is in most cases less than one percent and it may be concluded that the equation (2) can be applied for whole range of orthobaric state without any considerable error. This relation holds even for alcohols, which contain obviously associated molecules. Only for water it does not hold, because of the abnormal behaviour of its liquid phase.

Values of E used in the foregoing tables are approximately proportional to the critical volume V_k for normal liquids, as shown in Table 9. Consequently E should be an additive quantity, but the data are not sufficient to calculate out reliable additive constants for each atom or radical.

TABLE 9.

Substance	E	$V_{P=\infty}$	E/V_k	A	$T_k/\sqrt{AP_k}$
Hydrogen	4.20	—	0.0596	3958	0.148
Oxygen	9.68	—	0.130	18160	0.162
Nitrogen	12.8	—	0.142	17520	0.164
Argon	10.3	—	0.137	17440	0.165
Carbon dioxide	22.8	—	0.240	33600	0.195
Isopentane	53.8	—	0.175	204300	0.174
Normal octane	87.0	—	0.177	355900	0.180
Benzene	41.5	—	0.162	218500	0.174
Hexamethylene	52.6	—	0.171	249700	0.175
Chlorobenzene	50.15	—	0.163	292700	0.175
Carbon tetrachloride	44.3	—	0.161	232000	0.172
Stannic chloride	58.43	—	0.166	307600	0.176
Methyl acetate	37.8	—	0.166	173700	0.178
Ethyl formate	37.8	—	0.165	174000	0.178
Propyl formate	46.5	—	0.163	232700	0.173
Methyl butylate	59.2	—	0.174	276700	0.179
Ethyl ether	50.0	51.4	0.174	185600	0.181
Methyl alcohol	24.4	23.1	0.207	78950	0.205
Ethyl alcohol	37.8	33.6	0.226	105900	0.200
Propyl alcohol	48.6	—	0.221	143500	0.197
Acetic acid.	30.0	—	0.175	151100	0.202

As shown in Table 9 the ratio E/V_k is 0.169 in the mean, or E is about $V_k/6$ for normal liquids. For carbon dioxide and other abnormal liquids like alcohols the ratio is considerably higher and amounts to 0.21—0.24. The volume correction b in van der Waals' equation being about $V_k/4$ when extrapolated to $T=0$, so it can be said that E is about $2/3 \cdot b$ for almost all normal liquids.

G. Tamman(1) has given the following isothermal equation for liquids under high pressure :

$$(V - V_{P=\infty})(K+P) = A_T K.$$

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(1) *Ann. Phys.*, **87** (1912), 975.

In this equation $V_{P=\infty}$ and K are constants independent of temperature and pressure, while A_T is independent of pressure but varies with temperature. $V_{P=\infty}$ is the molecular volume of the liquid under infinitely large pressure, and is given in the third column in Table 9, which has been obtained by interpolation. As is seen in the table the value of E is nearly equal to $V_{P=\infty}$ of Tammann.

For constant A, there exists a relation that the ratio $T_k/\sqrt{AP_k}$ is roughly constant for normal liquids. For abnormal liquids this ratio is larger than that for normal one, but for alcohols it approaches to that of normal liquids, as the number of carbon atoms in the molecules increases.

We can thus formulate as follows :

$$E=0.17\ V_k \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

$$A=32.3\frac{T_k^2}{P_k}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

Putting $T/T_k=\theta$ and $V/V_k=\varphi$, we obtain from equations (5), (6) and (2),

$$R\theta\ln\frac{\varphi_g}{\varphi_l}=32.3\,\frac{T_k}{P_kV_k}\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right)=1.47\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right).$$

This equation is of reduced form and is in accord with the theory of the corresponding state, as the ratio P_kV_k/T_k is almost universal for normal liquids.

By slightly modifying the equation (2) we obtain

$$q=RT\ln V_g+\frac{A}{V_g-E}=RT\ln V_l+\frac{A}{V_l-E}\cdots\cdots(7)$$

each side having V_g or V_l only. By actual calculation, it was found that q is a linear function of temperature, thus

$$q=C+BT\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(8)$$

B, the temperature coefficient of q, is very small for normal liquids, and has considerable negative values for abnormal liquids. This enables us to calculate every pair of orthobaric densities as two roots of the equation (8), provided the values of C and B are known.

Next, an equation for vapour pressure at low temperatures can be derived from equation (2). By neglecting $A/(V_g-E)$, and regarding the vapour as an ideal gas, we can transform the equation (2) as follows :

$$\ln P=\ln\frac{RT}{V_l}-\frac{1}{RT}\,\frac{A}{V_l-E}\cdots\cdots\cdots\cdots(9)$$

where vapour pressure P is given by the molecular volume of the liquid. As an example of the verification of this equation, the data for ethyl ether are given in the following table.

TABLE 10.

Temp. C.	Vapour press. (obs.) mm.	Vapour press. (calc.) mm.	Observer
−101°.3	0.058	0.0535	Mündel
− 95.2	0.118	0.118	„
− 88.1	0.270	0.276	„
− 81.0	0.584	0.588	„
− 75.8	0.953	1.18	Drucker and Kangro
− 64.4	2.77	2.81	„ „
− 57.3	5.12	5.18	„ „
− 44.2	14.17	13.6	„ „
− 35.0	26.95	25.4	Taylor and Smith
− 32.4	31.93	30.1	„ „
− 20	63	63.7	Ramsay and Young
− 10	111.8	110	„ „
0	184.9	181	„ „

The vapour pressure calculated by the equation (9) agrees well with the observed value even at the temperature more than 100 degrees below the room temperature.

Sammary.

1. There exists a relation

$$RT\ln\frac{V_g}{V_l}=A\left(\frac{1}{V_l-E}-\frac{1}{V_g-E}\right)$$

between orthobaric densities for normal and abnormal liquids.

2. By modifying the above equation, we obtain

$$RT\ln V_g+\frac{A}{V_g-E}=RT\ln V_l+\frac{A}{V_l-E},$$

each side being proved to be a linear function of temperature.

3. For constants A and E it was found that $A=32.3\dfrac{T_k^2}{P_k}$ and $E=0.17 V_k$ for normal liquids. E is, therefore, an additive quantity if V_k is additive.

4. By dint of the relation for constants A and E mentioned above, we have a reduced equation

$$R\theta\ln\frac{\varphi_g}{\varphi_l}=1.47\left(\frac{1}{\varphi_l-0.17}-\frac{1}{\varphi_g-0.17}\right).$$

5. For lower temperatures, we have derived a vapour pressure equation

$$\ln P = \ln \frac{RT}{V_l} - \frac{1}{RT} \frac{A}{V_l - E} .$$

The author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance throughout the present research.

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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. III.
THE ACTION ON PRIMARY ALIPHATIC ALCOHOLS.

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Sabatier(1) and his co-workers have already described the dehydration of some primary alcohols by the catalytic action of alumina and other metallic oxides, and the experiments were reported by Ipatiew,(2) especially with regard to the formation of ethers and hydrocarbons of the olefine series from alcohols in presence of alumina, at different temperatures. The present experiment, therefore, was attempted by the writer to find some relation in the catalytic behavior on some aliphatic alcohols, between Japanese acid earth and alumina.

1. Methyl Alcohol. Forty gr. of methyl alcohol purified with lime, b.p. 65–66°, was passed on Japanese acid earth heated at 150°, 200°, 250°, 300°, 350° and 500° respectively at a rate of 14.4 c.c. per hour with a current of air or carbon dioxide gas. Of the reaction products, the qualitative and quantitative determinations of the gaseous substances were made by absorbing with bromine water, and also by the combustion method as usual, and of the liquid one by physical and chemical properties after fractional distillation. The results are shown in the following table.

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(1) Sabatier and Mailhe, *Bull. Soc. Chim.*, (4), **1** (1907), 137, 341, 524 & 773.

(2) Ipatiew, *Ber.*, **36** (1903), 1993.

TABLE 1.

Temp.	Gas	Alcohol & water		Gaseous subst.		Para-form-aldehyde
		gr.	d^{20}_{20}	C_2H_4 (%)	CO (%)	
150°	Air CO_2	20 30	0.8592 0.8250	0.71 1.29	4.86 9.77	
200°	Air	13	0.9603			
250°	Air CO_2	13 25	0.9520 0.8512	1.09 0.33	5.83 0.91	
300°	Air	17	0.9535	6.96	7.41	Trace
350°	Air CO_2	21 27	0.9772 0.9601	28.05 12.55	4.03 0.36	0.03 (m.p. 157°) —
500°	Air	23	0.9905	26.73	5.20	0.06

The occurrence of formaldehyde and of its polymer para-aldehyde in the reaction product was confirmed by the characteristic odour and by the physical properties (m.p. 157–160°). The formation of ethylene, as is seen in the table, is favorable with high temperature, and the yield of carbon monoxide is greater in presence of air than in carbon dioxide.

The same experiment which was undertaken on methyl alcohol, has been extended to ethyl alcohol, isobutyl (b.p. 108°; $d^{15}_{15}=0.8075$) and isoamyl alcohol (b.p. 130–132°; $d^{15}_{15}=0.8189$; $[\alpha]^{18}=2^{\circ}19'$), and the latter one, as will be seen from its physical constants, contains some active amyl alcohol as an impurity.

2. **Ethyl Alcohol.** Ethyl alcohol purified with silver oxide,(1) was examined by the same was as the case of methyl alcohol.

TABLE 2.

Alcohol gr.	Temp.	Vel. of alcohol c.c./h.	Alcohol & water gr.	Ether %	Ester %	Aldehyde %	C_2H_4 %
40	150°	21.26	25.27	5.73	14.73	about 1	1.72
"	200°	21.26	—	12.31	—	29.27	38.50
"	200°	51.87	11.40	53.02	—	2–3	15.30
"	250°	53.40	—	21.36	—	—	51.61
"	350°	17.83	—	—	—	—	95.71

The yield of ethylene from the alcohol, depends not only upon the rate of passing on catalyst, but on the reaction temperature. The formation of ether, which is due to the dehydration of alcohol as in the case of ethylene-formation, shows a maximum in yield at 200°. The oxidation of alcohol to aldehyde, the polymerisation of the oxidized substance into para-aldehyde (b.p. 120–124°) and the formation of ethyl acetate due to the dismutation of the aldehyde, were confirmed to occur simultaneously by the isolation of these reaction products in a fairly pure state.

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(1) Dulap, *J. Am. Chem. Soc.*, **28** (1906), 395.

3. Isobutyl Alcohol. In the case of isobutyl alcohol, isobutylene and β-butylene are the main reaction products as mentioned by Ipatiew⁽¹⁾ and Senderens⁽²⁾ in the catalytic action of alumina on the alcohol, and dibutyl ether (b.p. 140.9°; $d_{15}^{15}=0.7685$) and di-isobutylene (b.p. =110–113°; $d_{15}^{15}=0.7347$) were confirmed to occur in the reaction product by determining the physical constants of the corresponding fractions mentioned in the following table.

TABLE 3.

Temp.	Vel. of alcohol c.c./h.	Butylenes %	Liquid reaction products.	
			ice cooled gr.	water cooled gr.
150°	15	19.58	0.027 (0.11%)	4.807
250°	”	57.25	0.229 (0.97%)	1.934
350°	”	64.96		1.196

Temp.	Fraction	Yield gr.	d_{20}^{20}	n_D^{20}	Remark
150°	to 82°	2.9	0.7472	1.39619	
	103–105°	1.1	0.7840	1.39221	
	105–107°	0.7	0.7852	1.39932	
	107–140°	0.5	0.7794	1.40108	
	140–145°	0.3	0.7639	1.42310	Mostly di-butyl ether
	145–150°	0.9	0.7674	1.43287	
	above 200°	1.2	0.7829	1.43783	
250°	60–62°	1 drop			
	62–85°	—			
	85–110°	6 drops			
	110-113.5°	0.7	0.7344	1.41500	Di-isobutylene
	114–181°	0.6	0.7994	1.45287	
	Residue	0.3			
350°	to 90°	—			
	90–110°	0.2	0.7724	1.43887	
	Residue	0.5	0.8298	1.44326	

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(1) Ipatiew, *Ber.*, 36 (1903), 1993.

(2) Senderens, *Bull. Soc. Chim.*, (4), 1 (1907), 692.

4. Isoamyl Alcohol. With amyl alcohol, as will be seen in Table 4, amylenes (isopropyl ethylene, methyl-ethyl-ethylene and trimethyl-ethylene), diamyl ether and diamylenes were confirmed to occur as usual in the lower fractions of the reaction product, and the yield of these substances tends to increase with the reaction temperature.

TABLE 4.

Temp.	Fraction	Yield gr.	d^{15}_{15}	n^{20}_{D}	Remark
150°	40–45°	0.7	0.6438(0°)	1.35836	Amylenes
	45–50°	0.9	—	1.35978	
	50–57°	1.1	0.7320(0°)		
	59–65°	1.1	0.7450(0°)		
	65–70°	1.4	0.7411(0°)	1.37639	
	70–75°	1.2	0.7444(0°)	1.37397	
	75–115°	0.2	0.7874(0°)		
	115–125°	0.3	0.8109(0°)		Diamylenes & amyl alcohol
	125–130°	10.8	0.8012	1.40867	
	130–135°	3.6	0.8027	1.40727	
	135–137°	5.7	0.7988	1.40925	
	170–175°	2.0	0.7783	1.41232	Diamyl ethers
	175–180°	1.3	0.7757	1.41331	
	180–185°	2.2	0.7875	1.41580	
	to 220°	2.2	0.7872	1.43341	
200°	28–33°	1.0		1.37252	Amylenes
	33–37°	2.0		1.37518	
	125–135°	1.4	0.7664	1.41820	Diamylenes & amyl alcohol
	150–160°	2.5	0.7743	1.42120	
	160–170°	0.5	0.7557	1.42440	Diamyl ethers
	170–177°	0.6	0.7693	1.45287	
	above 180°	2.9	0.8101		

TABLE 4. (Continued)

Temp.	Fraction	Yield gr.	d_{15}^{15}	n_D^{20}	Remark
250°	28-33°	2.0	0.6606	1.37667	Amylenes
	33-37°	3.4	0.6659	1.37931	
	37-90°	10 drops			
	90-100°	0.6	0.7658		
	120°(±1°)	0.4	0.7828		Diamylenes & amyl alcohol
	125-150°	0.7	0.7818		
	150-160°	1.2	0.7868	1.45797	
	160-200°	0.8	0.8168	1.48968	
	200-210°	0.6	0.8679	1.51153	
300°	28-33°	1.9	0.6646	1.37683	Amylenes
	33-37°	5.6	0.6672	1.37931	
	37-40°	1.2	0.6745	1.38186	
	40-110°	1 drop			
	110-120°	0.4	0.7618	1.42940	Diamylenes
	120-150°	3 drops			
	150-160°	1.1	0.8050	1.45507	
	Residue	1.3	0.8893	1.50831	
350°	28-33°	3.0	0.6590	1.37509	Amylenes
	33-37°	4.0	0.6700	1.37742	
	37-40°	1.3	0.6721	1.38243	
	40-110°	5 drops			
	110-120°	0.6	0.7848	1.44195	
	120-130°	4 drops			Diamylenes
	130-140°	1.1	0.8238	1.46949	
	140-142°	0.9	0.9010	1.49871	
500°	20-40°	1.0	0.5885		Amylenes
	40-140°	13 drops			
	140-144°	1.2	0.8720	1.49871	Diamylenes

By the contact action of Japanese acid earth, primary alcohols of the aliphatic series yield unsaturated hydrocarbons and ethers as in the case of the catalytic action of alumina, and also aldehydes and esters. Both the dehydration of alcohols and the polymerisation of unsaturated hydrocarbons and aldehydes, as we noticed in the present research, resulted in excellent yields at high temperature. The oxidation of alcohols and the dismutation of the oxidized substance, which occur with this catalyst but not with alumina, are favorable at low temperatures.

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SOME DERIVATIVES OF HYDROXYPHENYLGLYCINE.(1) I.

By Kotaro SHIMO.

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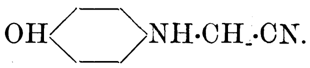
Alkyl and Aryl Derivatives of Hydroxyphenylglycine Nitrile.

1. p-Hydroxyanilidoacetonitrile (p-Hydroxyphenylglycine nitrile),



Bucherer and Gtolée(2) synthesized some derivatives of p-hydroxyphenylglycine nitrile from potassium cyanide, p-aminophenol hydrochloride and acetone or benzaldehyde, and p-hydroxyphenylglycine nitrile has recently been synthesized by Galatis(3) by the condensation of p-aminophenol with formaldehyde and potassium cyanide in presence of sodium sulphite.

p-Hydroxyanilidoacetonitrile was obtained applying the principle used for the synthesis of anthranilidoacetonitrile by E. Kohner(4) from p-aminophenol, formaldehyde and potassium cyanide with 89–95% yield of the theory.

Twenty one gr. of finely powdered p-aminophenol was mixed with 50c.c. of glacial acetic acid to form a homogeneous paste, cooled with ice-water and then 20 gr. of finely powdered potassium cyanide and 20 c.c. of formaline

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(1) This paper was read before the annual meeting of the Chemical Society of Japan, April 6th 1924 and at the monthly meeting, May 1st. 1926 and published in the *Osaka Kōgyōshikensho Hōkoku* (in Japanese), 5 (1924), No. 7, and will be published in the same publication, 7, (1926).

(2) *Ber.*, 39 (1906), 986.

(3) *Helvetica Chim. Acta*, 4 (1921), 574.

(4) *J. prakt. Chem.*, (2), 63 (1901), 392 ; also refer D.R.P. 117924; Friedländer, " Fortschritte der Teerfarben-fabrikation," VI (1900–1902), 572.

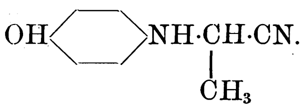
(Japanese Pharmacopœia) were added alternately in a portion of 2–3 gr. After all were added, the mixture was warmed at 70–80° for half an hour on a water bath and left to stand over night. On adding some water the nitrile was deposited, which was collected after cooling at 0°. The yield was 20 gr. The nitrile that remained in the mother liquor was extracted with ether, and after evaporating off the solvent there remained crystals weighing 5.5 gr. Total yield was 89% of the theory.

The condensation of p-aminophenol with formaline and potassium cyanide was carried out in aqueous solution ; 30 gr. of p-aminophenol hydrochloride was dissolved in 140 c.c. of water, and to a mixture of 17 c.c. of formaline (Japanese Pharmacopœia), 75 gr. of 20% aqueous potassium cyanide solution was added drop by drop with constant agitation and cooling it with ice-cold water during the reaction, thereby a voluminous greyish white precipitate was deposited. It was then warmed up to 60–70° and after all of the precipitate was dissolved the solution was cooled, and p-hydroxyphenylglycine nitrile was deposited as large transparent platy crystals. The yield was 29.1 gr. which corresponds to 95% of the theory. It melts at 103–104° (uncorr.) while Galatis described 100° as its melting point.

It gives a transient fuchsin-red coloration described by Galatis and also the same coloration with silver nitrate producing white precipitate, with ammoniacal silver nitrate a yellow color which changes to yellowish brown colloidal solution then greyish black precipitate, yellowish red coloration followed by effervescence with concentrated nitric acid, red coloration with Millon's reagent without warming, and orange coloration with potassium ferricyanide. On analysis, it gave the following results :

0.1619 gr. subst. gave 0.3859 gr. CO_2 and 0.0841 gr. H_2O. 0.0567 gr. subst. gave 8.85 c.c. N_2 (11.5°, 762 mm.). (Found : C = 65.01 ; H = 5.77 ; N = 18.86. $C_8H_8ON_2$ requires C = 64.87 ; H = 5.41 ; N = 18.92%).

2. p-Hydroxyanilidomethylacetonitrile,

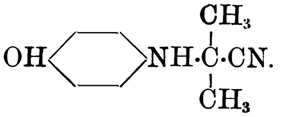


$OH\cdot C_6H_4\cdot NH\cdot \underset{CH_3}{\underset{|}{CH}}\cdot CN.$

It was prepared from 10.8 gr. of p-aminophenol, 10 gr. of potassium cyanide, and 10 c.c. of 50% acetaldehyde in a manner described for the preparation of p-hydroxyanilidoacetonitrile. The yield of the crude nitrile was 7.6 gr. It was recrystallised from ether-ligroin solution in fine white microscopic leaflets which melt at 111–112° (uncorr.).

0.1220 gr. subst. gave 0.2985 gr. CO_2 and 0.0687 gr. H_2O. 0.1025 gr. subst. gave 14.85 c.c. N_2 (10°, 759.3 mm.). (Found : C = 66.73 ; H = 6.23 ; N = 17.54. $C_9H_{10}ON_2$ requires C = 66.67 ; H = 6.17 ; N = 17.28%).

3. p-Hydroxyanilidodimethylacetonitrile,

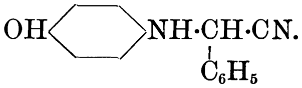


$$\mathrm{OH}\langle\quad\rangle\mathrm{NH}\cdot\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\cdot\mathrm{CN}.$$

This substance was obtained from 5.4 gr. of p-aminophenol, 5 gr. of potassium cyanide and 5 c.c. of acetone in 12 c.c. of glacial acetic acid. The yield was 7.4 gr. The purified substance is fine snow-white leaflets and melts at 140–142° while Bucherer and others described 137° as its melting point.

0.1246 gr. subst. gave 0.3104 gr. CO_2 and 0.0764 gr. H_2O. 0.1044 gr. subst. gave 13.9 c.c. N_2 (10°, 763.7 mm.). (Found: C=67.94; H=6.81; N=16.25. $C_{12}H_{12}ON_2$ requires C=68.18; H=6.82; N=15.91%).

4. p-Hydroxyanilidophenylacetonitrile,

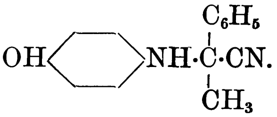


$$\mathrm{OH}\langle\quad\rangle\mathrm{NH}\cdot\underset{\mathrm{C_6H_5}}{\mathrm{CH}}\cdot\mathrm{CN}.$$

From 5.4 gr. of p-aminophenol, 3.5 gr. of potassium cyanide dissolving in 20 c.c. of water and 5 gr. of benzaldehyde in 50% acetic acid solution, 9.5 gr. of crude nitrile was prepared which recrystallized from luke warm benzene. The pure nitrile was yellow colored small needle-shaped crystals melting at 122–124° (uncorr.), while Bucherer and others described 113–114° as its melting point.

0.1034 gr. subst. gave 0.2839 gr. CO_2 and 0.0512 gr. H_2O. 0.1498 gr. subst. gave 16.0 c.c. N_2 (12.5°, 761 mm.). (Found: C=74.88; H=5.50; N=12.85. $C_{14}H_{12}ON_2$ requires C=75.00; H=5.36; N=12.50%).

5. p-Hydroxyanilidophenylmethylacetonitrile,



$$\mathrm{OH}\langle\quad\rangle\mathrm{NH}\cdot\overset{\mathrm{C_6H_5}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\cdot\mathrm{CN}.$$

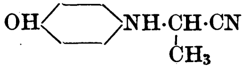
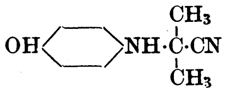
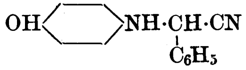
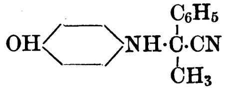
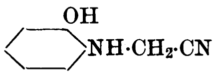
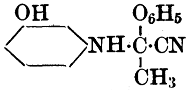
Twelve c.c. of glacial acetic acid, 5.4 gr. of p-aminophenol, 5 gr. of potassium cyanide and 10 gr. of acetophenone were treated in a similar manner as described in previous cases and 11.4 gr. of crude nitrile was obtained. It was purified from dilute alcoholic solution and melts at 128–130° (uncorr.).

0.1196 gr. subst. gave 0.3306 gr. CO_2 and 0.0674 gr. H_2O. 0.1044 gr. subst. gave 10.5 c.c. N_2 (11.5°, 757.7 mm.). (Found: C=75.39; H=6.26; N=12.08. $C_{15}H_{14}ON_2$ requires C=75.62; H=5.88; N=11.76%).

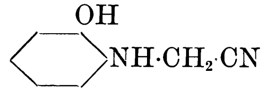
Alkyl or aryl derivatives of p-hydroxyanilidoacetonitrile described above, are soluble in both acid and alkali solutions (but aryl derivatives are insoluble in acid) and also in acetone, alcohol, ether, acetic ester, glacial acetic acid, chloroform and benzene, as I noticed in the case of p-hydroxyanilidoacetonitrile.

Other chemical behaviors of these substances towards ferric chloride, silver nitrate, Millon's reagent etc. are like those of the mother substance as will be seen in Table 1.

TABLE 1.

Substance.	Ferric chloride.	Silver nitrate.	Ammoniacal silver nitrate.	Conc. nitric acid.	Millon's reagent.	Potassium ferricyanide.
 m.p. 103–104°	fuchsin-red.	fuchsin-red producing white ppt.	yellow color → yellowish brown colloidal → greyish black ppt.	yellowish red.	red.	orange.
 m.p. 111–112°	brownish red.	pink → reddish violet producing white ppt.	brownish yellow colloidal → greyish ppt.	red.	yellow.	
 m.p. 140–142°	violet → chocolate color.	cobalt blue producing white ppt.	pale brownish grey colloidal → brownish grey ppt.	yellowish red.	yellow.	reddish brown.
 m.p. 122–124°	yellow.	yellow → brownish yellow ppt.	reddish orange colloidal.	reddish yellow.	yellow → colorless → brownish red.	
 m.p. 128–130°	bluish violet.	bluish violet producing white ppt.	greyish colloidal → brown → chocolate color.	yellowish red.	reddish orange.	
 m.p. 74–75°	yellowish red.	pale dirty red producing silver mirror accompanied with dirty brown ppt.	yellow → yellowish green → greyish black ppt.	red.	yellowish red.	reddish orange.
 m.p. 135–137°	brownish yellow.			yellowish brown.	red.	

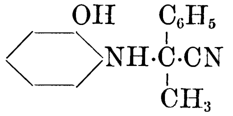
6. o-Hydroxyanilidoacetonitrile (o-Hydroxyphenylglycine nitrile),



o-Aminophenol reacts, in the same manner as p-isomer, in presence of glacial acetic acid with formaline and potassium cyanide producing o-hydroxyanilidoacetonitrile. 14.5 Gr. of the crude nitrile was actually obtained from 14.7 gr. of aminophenol. For the purification of the nitrile, the crude product was dissolved in ether, and to the ethereal solution ligroin was added until permanent turbidity began to occur, and the solution was left to evaporate slowly in vacuo or recrystallised from luke warm benzene. It melts at 74–75° (uncorr.), and is very easily soluble in ether, alcohol, acetone, acetic ester and glacial acetic acid, less so in chloroform, benzene and water but insoluble in ligroin. It is more easily saponifiable than the corresponding para compound ; when treated with warm water or dilute caustic alkalies, the evolution of ammonia is recognized. The color reactions of the nitrile are shown in Table 1.

0.1171 gr. subst. gave 0.2781 gr. CO_2 and 0.0608 gr. H_2O. 0.1058 gr. subst. gave 16.6 c.c. N_2 (8°, 766.4 mm.). (Found : C=64.77 ; H=5.81 ; N=19.29. C_8H_8ON requires C=64.87 ; H=5.41 ; N=18.92%).

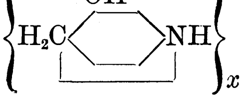
7. m-Hydroxyanilidophenylmethylacetonitrile,



This substance was obtained from 5.4 gr. of m-aminophenol, 12 c.c. of glacial acetic acid, 5 gr. of potassium cyanide and 9 c.c. of acetophenone in the manner described for the preparation of other nitriles. The yield was 5 gr. It was purified from ether-ligroin solution in fine white crystalline powder which melts at 135–137° (uncorr.). It is easily soluble in ether, alcohol, acetic ester and acetone, soluble in glacial acetic acid, less soluble in benzene and chloroform but insoluble in ligroin and water. The colour reactions of the nitrile are mentioned in Table 1.

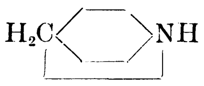
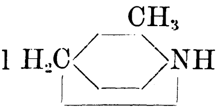
0.1093 gr. subst. gave 0.3047 gr. CO_2 and 0.0602 gr. H_2O. 0.1041 gr. subst. gave 10.2 c.c. N_2 (7.5°, 767.6 mm.). (Found : C=75.61 ; H=6.04 ; N=12.02. $C_{15}H_{14}ON_2$ requires C=75.62 ; H=5.88 ; N=11.76%).

8. Anhydro-p-amino-o-hydroxybenzylalcohol,



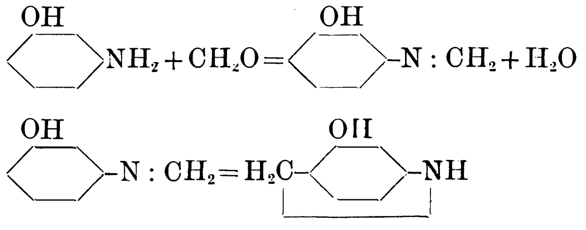
When 5.4 gr. of m-aminophenol was treated with 5 c.c. of formaline (Japanese Pharmacopœia) and 25 c.c. of 14% potassium cyanide solution in the manner described for the preparation of p-hydroxyanilidoacetonitrile, 6.3 gr. of a pale yellow amorphous powder was deposited which, after investiga-

tion of its insoluble nature in organic solvents and hydrochloric acid and melting point (does not melt under 300°), was regarded to be anhydro-p-amino-o-hydroxybenzylalcohol.

Moreover, the analytical results of the dried substance, and also the fact that anhydro-p-aminobenzylalcohol  and anhydro-p-amino-m-toluylalcohol  were synthesized from aniline and formaline, and o-toluidine and formaline, respectively,(1) give cause to presume it to be anhydro-p-amino-o-hydroxybenzylalcohol.

0.1340 gr. subst. gave 0.3430 gr. CO_2 and 0.0747 gr. H_2O 0.1159 gr. subst. gave 11.25 c.c. N_2 (8.5°, 761 mm.). (Found: $C=69.28$; $H=6.19$; $N=11.84$. C_7H_7ON requires $C=69.39$; $H=5.82$; $N=11.57\%$).

As to the formation of this substance, methylene-p-aminophenol would be formed as an intermediate reaction product from m-aminophenol and formaline, which soon converts to anhydrobenzylalcohol derivatives by the intermolecular rearrangement, before hydrocyanic acid enters into the condensation with the former hypothetical compound, as may be represented by the following scheme:



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Daini, Osaka.

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(1) D.R.P., 95184; Friedländer, "Fortschritte der Teerfarben-fabrikation," IV (1894-1897), 52; *Ber.*, 33 (1900), 252.

DETERMINATION OF HIGH TEMPERATURE BY THE EFFUSION AND THE TRANSPIRATION OF GAS.

By Yohei YAMAGUCHI.

Received August 28, 1926. Published October 28, 1926.

The rates of flow of gases at high temperatures were studied by Emich(1) for the determination of gas densities. I have undertaken some experiments to test whether such a phenomenon can be utilized for the determination of high temperature or not.

1. **The Relation between the Temperature and the Rate of Effusion.** The apparatus used for the measurement of the rate of effusion is shown in Fig. 1. On the stem of a glass vessel resembling Ostwald's viscosimeter, two marks A and B were etched, the volume between them being about 100 c.c. After the bulb was filled with a certain quantity of petroleum of high boiling point (215–225°), the lower part of the vessel is immersed in a thermostat at 25°. T is a quartz tube having a small opening at its end through which the gas effuses and is placed in an electric furnace. When the temperature of the tube became constant, the stop-cock C is opened and a certain quantity of dry air is blown into the system by means of D in order to push

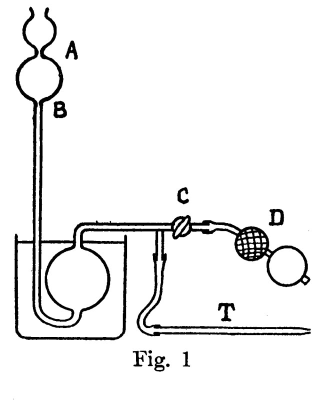

Fig. 1

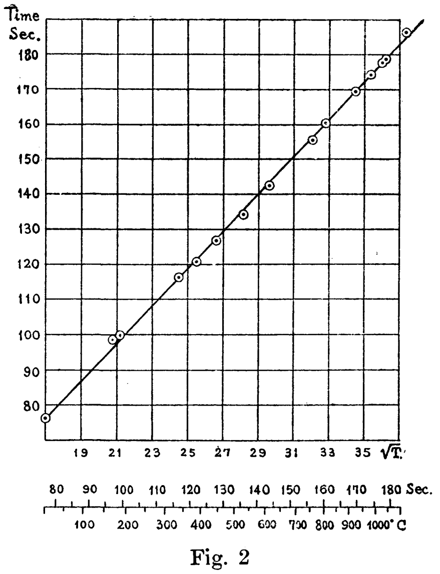

Fig. 2

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(1) Emich, *Monatsh.*, 24 (1903), 747; 26 (1905), 505.

up the petroleum above the mark A. Hereupon the stop-cock is closed and the time in which the petroleum falls down from A to B is measured. The relation between the measured time and the temperature is shown in Table 1⁽¹⁾.

TABLE 1.

Time in sec. (t)	Temp. C°.	Abs. temp. (T)	$\log T$	$\sqrt{T}$	$t_{calc.}$
76.4	17	290	2.4624	17.03	75.4
*115.8	328	601	2.7789	24.52	(115.8)
126.6	434	707	2.8494	26.59	127.0
142.9	605	878	2.9435	29.63	143.4
*170.0	922	1195	3.0774	34.57	(170.0)
177.9	1033	1306	3.1158	36.13	178.4
185.5	1125	1398	3.1456	37.40	185.3

Fig. 2 shows that there is a linear relation between the time (t) and the square root of the absolute temperature (T). Thus we can put,

$$t=a+b\sqrt{T} \cdots\cdots\cdots\cdots\cdots\cdots(1)$$

Taking out two pairs of observed values and calculating the constants a and b, we obtain, $t=5.393\sqrt{T}-16.44$. The times of effusion are calculated by this equation from the observed temperatures and are shown in the last column of Table 1. The calculated times are in good agreement with the observed ones.

Theoretical. The definite quantity of gas corresponding to the volume between the marks A and B, will expand to a larger volume at the opening of the quartz tube where the temperature is high. Hence if the velocity of effusion be independent of temperature, the time of effusion (t) is proportional to the absolute temperature (T),

$$t \propto \text{volume} \propto T \cdots\cdots\cdots\cdots\cdots\cdots(2)$$

Now the time of flow of gases by effusion under a given pressure difference is also inversely proportional to the mean velocity (v) of the gas molecules, and the mean velocity is, as is well known, proportional to the square root of the absolute temperature,

$$t \propto \frac{1}{v} \propto \frac{1}{\sqrt{T}} \cdots\cdots\cdots\cdots\cdots\cdots(3)$$

Combining (2) and (3), we have,

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(1) More detailed data were published in the *Journal of the Chemical Society of Japan*, 43 (1922), 1,

$$t \infty \sqrt{T}, \qquad \text{or} \qquad t=b\sqrt{T} \cdots\cdots\cdots\cdots\cdots (4)$$

where b is a constant. The constant a in the empirical equation (1) may be considered to be a correction term to the equation (4) obtained by such a simple deduction.

2. The Relation between the Temperature and the Rate of Transpiration. High temperatures can also be determined by measuring the rate of transpiration of gases through a capillary tube of quartz. The apparatus employed for the purpose is similar to that used above, excepting that the quartz tube for effusion is now replaced by another quartz tube of about 3 mm. diameter, one end of which is elongated so as to form a capillary. Some of the data obtained from the experiments are shown in Table 2.

TABLE 2.

Time in sec. (t)	log t	Temp. C°.	Abs. temp. (T)	log T	$T_{\text{calc.}}$
61.0	1.7853	20.5	293.5	2.4676	283
79.4	1.8998	125.5	398.5	2.6004	395
* 94.2	1.9741	200.2	473.2	2.6751	478
116.7	2.0671	333	606	2.7822	599
*151	2.1790	487	760	2.8808	767
212	2.3263	739	1012	3.0051	1025
*241	2.3820	848	1121	3.0496	1132
264.2	2.4219	929	1202	3.0799	1211
300	2.4771	1046	1319	3.1202	1321

The value of log T can well be represented by an equation of the second order of log t, thus

$$\log T=a+b \log t+c\,(\log t)^2 \cdots\cdots\cdots\cdots\cdots\cdots (5)$$

Evaluating the constants a, b and c from three data marked with asteriscs in Table 2, we get the following empirical equation,

$$\log T=-1.0967+2.7376 \log t-0.4178\,(\log t)^2 \cdots\cdots (6)$$

The values of $T_{\text{calc.}}$ in Table 2, which were obtained from this equation, are in good agreement with the observed values.

3. The Relation between the Temperature and the Pressure of Gas Transpirating at a Definite Rate. The temperature of transpirating gas can also be determined by measuring the pressure necessary to keep a constant rate of flow of the gas. The apparatus shown in Fig. 3 was used for the purpose. If water is allowed to run into the bottle A from the tube B, the air in

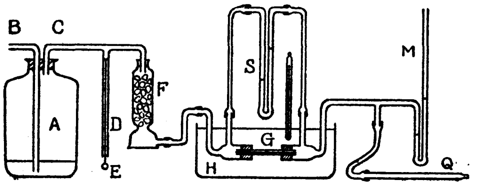

Fig. 3

A, being replaced by the water, will be expelled from the tube C under a certain pressure. The quantity of the air flowed out through the tube C could be controlled by regulating the water supply and by moving a copper wire E inserted in a capillary tube D. F is a drying tower filled with $CaCl_2$. G is a capillary flowmeter immersed in a thermostat H of 25°. S and M are manometers for measuring the pressure difference. Q is a quartz tube of about 3 mm. diameter, one end of which is elongated so as to form a capillary. If a temperature elevation takes place at the capillary part of Q, then the velocity of the air stream which passes through the capillary will decrease. Consequently the pressure of the supplied air must be increased, in order to keep the quantity of the air allowed to pass through the capillary at a constant value. This increase of the pressure is read by the manometer M. Thus in carrying out the experiment, the temperature at the capillary part of the quartz tube Q and the pressure difference indicated by the manometer M should be read off, under the constant pressure difference of the manometer S. Potroleum of high boiling point was used for the manometer S and water for the manometer M. Two series of experiments have been performed, when the pressure difference indicated by the manometer S are 10 cm. and 20 cm. in petroleum column respectively. The adridged data are shown in Table 3. Taking $\log p$ and $\log T$ as coordinates, there is found a linear relation between them, as is shown in Fig. 4.

TABLE 3.

Press. diff. of flowmeter S, in cm. of petroleum.	Press. of air in cm. of water indicated by manometer M. (p)	$\log p$	Abs. temp. (T)	$\log T$	$p_{calc.}$	$T_{calc.}$
10	1.38	0.1399	290	2.4624	1.39	288
	2.52	0.4014	437	2.6405	2.52	437
	4.73	0.6749	675	2.8293	4.72	676
	7.37	0.8675	915	2.9614	7.33	918
	10.28	1.0120	1153	3.0618	10.24	1156
	14.42	1.1590	1478	3.1697	14.67	1461
20	3.92	0.5933	287	2.4579	3.96	285
	6.98	0.8439	439	2.6425	7.05	436
	10.12	1.0051	573	2.7582	10.12	573
	16.44	1.2159	828	2.9178	16.66	819
	26.28	1.4196	1160	3.0645	26.37	1157
	36.00	1.5563	1479	3.1700	36.67	1459

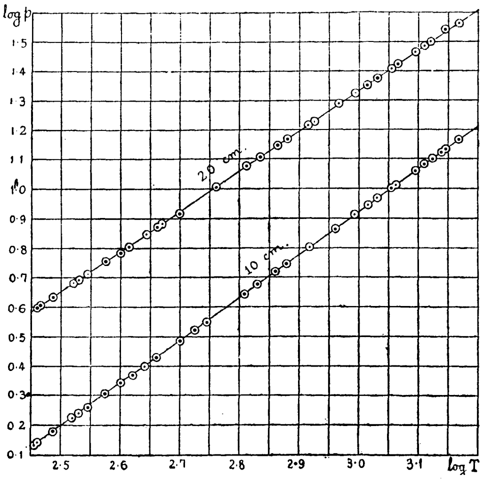

Fig. 4

Theoretical. In order to keep the quantity of the gas passing in a given interval through the quartz capillary always constant, notwithstanding the temperature of the capillary is elevated, the pressure of the gas must be increased. If we assume that all other conditions are constant, the gas must be compressed to its initial volume in order that the quantity of the transpirated gas should be kept invariably, and the pressure must change proportional to the absolute temperature, $p \infty T$. When the temperature is elevated, however, there takes place in the gas not only the increase of volume but also the increase of viscosity, so that the pressure must be increased a little more on account of the increase of viscosity. Let η be the viscosity, then we have

$$p \infty \eta, \quad \cdots\cdots\cdots\cdots(8)$$

therefore

$$\left.\begin{aligned} & p \infty \eta T, \\ & \frac{p}{p_0} = \frac{\eta T}{\eta_0 T_0} \end{aligned}\right\} \cdots\cdots\cdots\cdots(9)$$

or

According to Sutherland the relation between the viscosity and the absolute temperature T may be expressed by the following equation.

$$\frac{\eta}{\eta_0} = \left(\frac{T}{T_0}\right)^{\frac{1}{2}} \frac{1+\dfrac{c}{T_0}}{1+\dfrac{c}{T}} \cdots\cdots\cdots\cdots(10)$$

so

$$p = p_0\left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{1+\dfrac{c}{T_0}}{1+\dfrac{c}{T}} \cdots\cdots\cdots\cdots(11)$$

or

$$p = kT^{\frac{3}{2}}\left(1+\frac{c}{T}\right)^{-1} \cdots\cdots\cdots\cdots(12)$$

If c is small, and T is large in equation (12), we may put

$$\log p = \log k + \tfrac{3}{2} \log T \cdots\cdots\cdots\cdots(13)$$

This shows that the relation between log p and log T is linear, agreeing with the results shown in Fig. 4. Assuming a more general form,

$$\log p = a \log T + b \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (14)$$

two constants a and b being calculated by the method of least square from the observed data, thus :

Press. diff. on manometer S=10 cm., $a=1.4462$, $b=-3.4176$.

Press. diff. on manometer S=20 cm., $a=1.3582$, $b=-2.7414$.

In equation (13) which is derived from Sutherland's formula, the constant a is $\frac{3}{2}$. According to the above results, the value of a is smaller than $\frac{3}{2}$, but not very different from it. The values of the pressure p calculated by applying the above values of a and b in equation (14) are shown in the sixth column of Table 3. The calculated values are in good agreement with the observed values.

For the determination of temperature by measuring the pressure of gases, equation (14) must be transformed into the following form.

$$\log T = a' \log p + b' \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (15)$$

The values of a' and b' are found as follows.

Press. diff. on manometer S=10 cm., $a'=0.69146$, $b'=2.3632$.

Press. diff. on manometer S=20 cm., $a'=0.73623$, $b'=2.0183$.

The values of the temperature ($T_{\text{calc.}}$), corresponding to the observed p, calculated from equation (15) are shown in the seventh column of Table 3. Comparing the calculated values with observed values of T, we see that this method may be used for the determination of high temperatures with equally good result as other pyrometers.

It was thus shown that this method is applicable from common temperature up to about 1200°C. For lower temperatures experiments have not yet been undertaken. Assuming that the equation (12) could be applied also in this case, the linear equation (13) hardly be employed, as the factor $1+c/T$ becomes greater. The curve representing the required relation should deviate from the straight line which represents equation (13), as the temperature falls. As to the method of experiment, the apparatus shown in Fig. 3 can be employed without any alterlation for lower temperatures. At much lower temperatures, however, the pressure difference in the manometer M will be so small that the readings becomes very difficult. For this reason it will be better to modify the method of measurement, namely, to exchange the rôle of two manometers, and the difference in S should be read off, the difference in M being maintained to be constant, as the difference in S becomes greater according as the temperature falls.

Summary.

Three methods have been studied for the purpose of determining high temperature by the observation of the rate of flow of gas. In the first method the temperature is determined by the effusion of gas, time necessary for the escape of a definite quantity of gas being observed. The following equation can be applied for the range from the common temperature up to about 1000°,

$$t=a+b\sqrt{T}\ ,$$

where T is the temperature, t is the time of effusion of air which passes through a quartz opening, and a and b are constants. This method might be useful, as the apparatus employed for this purpose is very simple and the relation between time and temperature can be represented by a simple equation.

In the second method, the temperature is measured by the transpiration of gases through a quartz capillary, the time of flow being measured also in this case. In the range from common temperature up to about 1000°, the logarithms of the absolute temperature can be expressed as an equation of second order of the logarithms of the time.

In the third method, the increase of the pressure necessary to maintain a constant rate of flow was observed. In the range from the common temperature up to about 1200°, there was found a linear relation between the logarithm of pressure and that of absolute temperature.

In conclusion I express my best thanks to Prof. K. Ikeda for his kind guidance.

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THE RADIOACTIVITY OF THE RUBIDIUM EXTRACTED FROM THE LEPIDOLITE AND ZINNWALDITE OF JAPAN.

By **Satoyasu IIMORI** and **Jun YOSHIMURA.**

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Nothing is known about the radioactive serial genesis of potassium and rubidium, and there remain several important subjects still for decision. It has often been considered that the feebleness of their radioactivity might be ascribed to their inferior isotopes admixed, viz. K^{41} and Rb^{87}: According to this supposition the activity of these elements might not be always the same when the mineral source of the elements are different. A number of preparations of potassium salt of different origins were ever examined for the activity, and it was pointed out that a fixed result was consistently obtained(1); but on rubidium no study of this line has yet been made. In the present work, it was undertaken, therefore, to prepare the pure rubidium preparations from some Japanese lithia micas and to compare their activities with that of the Kahlbaum's preparation which is probably derived from the Stassfurt deposits.

Method of Separating the Rare Alkalies. The separation of the rare alkalies was effected by adopting a special procedure improved by the authors. The method was based upon the sparing solubility of caesium antimony chloride(2) and rubidium stannic chloride(3) in concentrated hydrochloric acid. On treating the dried solid mixture of alkali chlorides with concentrated hydrochloric acid (sp. gr., 1.185), the most part of sodium chloride, which is least soluble in hydrochloric acid, is first removed, and subsequently caesium and rubidium are precipitated in presence of potassium and lithium from the filtrate, one after another by adding suitable quantities of hydrochloric acid solutions of antimony chloride and stannic chloride respectively. After removal of the tin and antimony as sulphides, the final filtrate is evaporated up to dryness, and the residue which contains the chlorides of whole lithium and potassium as well as a trifling remainder of sodium, is now put together with the first residue of sodium chloride and used for the estimation of lithium, sodium and potassium which are quite readily separable by the usual method. In carrying out this process, the volume of solutions, in which the precipitations occur, is very important and notably influences every precipitations, especially that of caesium antimony chloride. The solubilities of all the alkali chlorides and double chlorides in concentrated hydrochloric acid (1.185), which are given in Table 1 and Table 2,

TABLE 1.

Approx. Solubility of Alkali Chlorides in Hydrochloric Acid (sp. gr., 1·185) at 16~17°C.

Chlorides.	Gr. chloride which are dissolved in 100 c.c. HCl.	C.c. HCl, in which 1gr. chloride dissolves
CsCl	55.3	1.8
RbCl	16.1	6.2
LiCl	31.3	3.2
KCl	1.1	90.0
NaCl	0.1	1000.0

TABLE 2.

Solubility of Double Chlorides in HCl (sp. gr., 1·185) at 20°C.

Double chlorides	Gr. double chloride which exists dissolved in 100 c.c. HCl solution.
$3CsCl \cdot 2SbCl_3$	0.4599 (=0.2416 CsCl or 0.2021 Cs_2O)
Rb_2SnCl_6	0.0194 (=0.0093 RbCl or 0.0072 Rb_2O)
K_2SnCl_6	0.1892 (=0.0689 KCl or 0.0435 K_2O)

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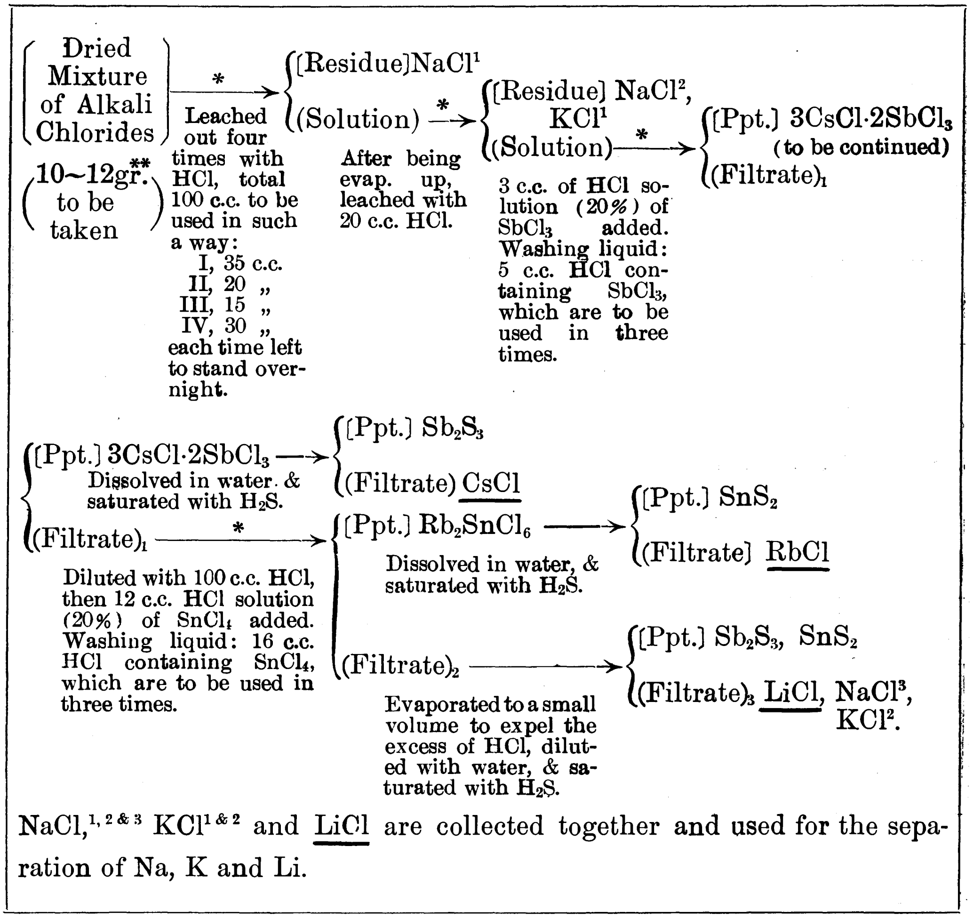
(1) N. R. Campbell, *Proc. Cambridge Phil. Soc.*, **14** (1908), 15.
W. Biltz & E. Marcus, *Z. anorg. Chem.*, **81** (1913), 369.

(2) R. Godeffroy, *Ber.*, **7** (1874), 376; *Liebig's Ann. Chem.*, **181** (1876), 176.

(3) S. P. Sharples, *Am. J. Sci.*, (2), **97** (1869), 178.

as well as the mutual effects upon solubilities were therefore determined, and a scheme of procedure was established. Table 3 illustrates the outline of the scheme. The vessels to be employed for the separation must strictly be avoided from moisture, consequently the asbestos filters, extracting flasks, etc. were used to kept in a large desicator. The process proved to give a quite satisfactory result.

TABLE 3.



* Asbestos filter is to be employed for the filtration.

** Limiting amounts (gr.) of chlorides to be taken for separation:—
CsCl: 0·5, RbCl: 1·5, NaCl: 2·0, LiCl: 5·0 and KCl: 5·0, viz. total: 14·0 gr.

The Rubidium Content of the Lithia Micas of Japan. Since the rubidium usually occurs associated with lithium, all available specimens of

Japanese lithia and lithia iron micas were preliminary analyzed for alkalies by the ordinary method of J. Lawrence Smith with the result shown in Table 4.

TABLE 4.

Micas analyzed		Li_2O(%)	Na_2O(%)	K_2O(%)
Tanokami zinnwaldite	large crystals, transparent with purple shade.	4.24	5.00	7.89
〃 〃	largec rystals, transparent with brown shade.	3.66	2.18	7.52
Naegi zinnwaldite	large crystals, transparent with brown shade.	2.31	5.82	8.35
Nagatori lepidolite	congregated mass of quartz and scaly mica.	2.49	3.20	9.13
〃 〃	〃 〃, a diff. lump.	1.94	2.70	6.71

For the extraction of rubidium the Tanokami zinnwaldite and Nagatori lepidolite were dealt with, and the separation was carried out according to the above mentioned method. The results obtained were as follows :

TABLE 5.

Micas	Amount taken (gr.)	Rb_2SO_4 yielded (gr.)	Rb_2O %
Tanokami zinnwaldite (1st sample):	60.11	0.6916	0.81
〃 〃 (2nd sample):	60.43	0.8538	0.98
Nagatori lepidolite :	60.05	0.8214	0.96

It has been proved spectrographically that all of these sulphate preparations contained no impurity but very small amount of caesium which could not be thrown down by antimony chloride in the course of separation. This amount of caesium contained in the preparations was so ascertained from the scale of procedure that it never exceeds 0.08% at most referred to to the sample.

The Radioactivity of the Rubidium Sulphate Preparations. The β-ray activity of these preparations was measured by means of a sensitive alpha-ray electroscope and compared with that of the Kahlbaum's preparation. The results obtained are set out in Table 6.

TABLE 6.

Sample	Thickness of layer(gr./cm.^{2})	Activity (div./hr.)	Comparison of activity
The β-ray standard (U_3O_8)	—	1425*	100
Rubidium sulphate preparation of Kahlbaum	0.0294	3.5 per gr.	0.246
Rubidium sulphate prep. from Tanokami zinnwaldite	0.0116	3.4 „	0.239
Rubidium sulphate prep. from Nagatori lepidolite	0.0256	3.6 „	0.253

* This is the limiting activity of the β-ray from the uranium oxide employed as the standard, corrected for the absorption by the aluminium foil of 0.05 mm. thickness used to cover the standard.

It will be seen that no marked difference in the activity of these preparations could be detected, the activities expressed per gr. in those layer thicknesses indicated in the above table having been directly compared with the limiting β-ray activity of the uranium oxide as the absorption coefficient of the prepatation for the β-ray from rubidium is unknown. Thus, it may be concluded that the activity of rubidium so far studied in the present work does not depend upon the mineral, from which the element has been extracted.

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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. IV. THE ACTION ON CYCLOHEXANOL AND ITS DERIVATIVES.

By **Harushige INOUE.**

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Chavanne and Roelan⁽¹⁾ have observed that cyclohexanol, by the contact action of alumina, was decomposed at 160° into cyclohexene and water, and the same chemical reaction of the alcohol was also noticed by Bouveault⁽²⁾ when clay was used as a catalyst at 300°. Japanese acid earth behaves as a catalyst, as mentioned in the previous articles of this subject,⁽³⁾ in a some-

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(1) Chavanne and Roelan, *Chem. Zentr.*, **80** (1909) I, 73.

(2) Bouveault, *Bull. Soc. Chim.*, [4] **3** (1908), 118.

(3) Inoue, this journal, **1** (1926), 157, 177 & 197.

what different way from alumina, clay or silica which were regarded as the principal constituents of the Japanese acid earth, and the present research was undertaken in the expectation of getting some different results, in some respects, from those mentioned by Chavanne and Roelan, and also by Bouveault.

The cyclohexanol used in the experiment, was prepared from pure phenol by catalytic reduction with reduced nickel and pure hydrogen under 20 atmospheric pressures at 180°, which shows: b.p. 135° under 84.6 mm.; m.p. below 18°; $d_{20}^{20}=0.9547$; $n_D^{20}=1.4650$.

Cyclohexanol(1) was passed with air, or CO_2 on the catalyst heated at 200° and 330° respectively, and the reaction product, which consisted of oily and water layers, was fractionated after being dried with anhydrous sodium sulphate as usual, and each fraction was determined its density and the index of refraction and the results are shown in Tables 1–4.

TABLE 1.

50.9 gr. of cyclohexanol yielded 23.4 gr. oil ($d^{20}=0.8143$) at 200°, in an atmosphere of air.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
80–82°	12.2	0.7971	1.44476
82–84°.5	4.7	0.8007	1.44070
85–90°	1.7	0.8045	—
above 90°	3.3	0.8942	1.48078

TABLE 2.

52 gr. of cyclohexanol yielded 26 gr. oil ($d^{20}=0.8362$) at 200°, in an atmosphere of CO_2.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
80–82°	6.6	0.7941	1.43622
82–84°.5	10.3	0.7962	1.43772
85–90°	0.7	0.8059	1.44165
90–225°	1.4	0.8774	1.47215
Residue	3.3	0.9044	1.48881

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(1) Inoue, *J. Soc. Chem. Ind. Japan*, 27 (1924), 553.

TABLE 3.

51.4 gr. of cyclohexanol yielded 32.6 gr. oil ($d^{20}=0.8123$) at 330°, in an atmosphere of air.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
71–73°	3.2	0.7512	1.41177
73–75°	8.1	0.7536	1.41321
75–80°	3.3	0.7563	1.41510
80–93°	1.6	0.7741	1.42140
93–215°	3.9	0.8896	1.55273
Residue	6.6	0.9644	1.56521

TABLE 4.

49.7 gr. of cyclohexanol yielded 32.8 gr. oil ($d^{20}=0.8065$) at 330°, in an atmosphere of CO_2.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
71–73°	2.2	0.7492	1.41282
73–75°	11.5	0.7518	1.41326
75–80°	3.6	0.7558	1.41510
80–93°	1.5	0.7678	1.42370
93–215°	3.7	0.8975	1.50522
Residue	6.4	0.9646	1.55198

As will be seen in Tables 1 and 2 the fractions with b.p. 80–82°, and b.p. 82–84°.5 which are main parts of the reaction product obtained at 200°, as indicated by the physical constants, seem to composed of the cyclohexene resulting by the dehydration of cyclohexanol, which was confirmed by isolating adipic acid (m.p. 153-154°), from the oxidation product of the fractions with nitric acid following the directions denoted by Markonikoff.(1)

While the reaction product resulting at 330°, consisted principally of the fraction with b.p. 73–75° which agrees in density and index of refraction with methyl-cyclopentane isolated by Markonikoff(2) from the low-boiling fractions of Caucasian petroleum, and also by Young(3) from American oil. For the confirmation of the fraction, it was subjected to the oxidation with nitric acid according to the directions of Aschan,(4) and acetic and succinic acids with a

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(1) Markonikoff, *Ann.*, **302** (1899), 27.
(2) Markonikoff, *Ber.*, **30** (1897), 1223.
(3) Young, *J. Chem. Soc.*, **73** (1898), 906.
(4) Aschan, *Ber.*, **31** (1898), 1804.

neutral substance of camphor-like odour, m.p. 176–178°, and of unknown chemical nature, were isolated from the reaction product, and the two acids were confirmed by the characteristic odour and melting point determination (m. p. 183°) respectively.

The formation of methyl-cyclopentane from cyclohexanol, by the contact action of the acid earth at 330°,. with decrease in the carbon ring C_6 to C_5, is completely analogous to the so-called rearrangement, the "retropinacoline rearrangement," suggested by Tiffeneau,(1) of alcohols of the cyclohexane series. Such conversion of the cyclohexane ring into the cyclopentane ring was carried out previously by Markonikoff(2) with amino cyclohexane and hydrogen iodide, and by Zelinski(3) with iodocyclohexane.

The assumption of an intermediate formation of cyclohexene, in the way, from cyclohexanol to methyl-cyclopentane, was examined experimentally by transforming the former compound isolated from the reaction product which was obtained by passing cyclohexanol on the earth at 200°, into methyl-cyclopentane.

From 40.8 gr. of the fraction (b.p. 82–84°) mentioned in Table 1, by passing on the earth heated at 330°, 29 gr. of oil ($d^{20}_{20}=0.7942$), 0.5 gr. of ethylene, and 1.2 gr. of water were obtained. The oily reaction product was fractionated into the following 6 portions, and each fraction was studied for density and index of refraction.

TABLE 5.

Fraction	Yield gr.	d^{20}_{20}	n^{20}_{D}
70–73°	3.8	0.7464	1.41044
73–75°	3.4	0.7533	1.41301
75–77°	4.3	0.7567	1.41441
77–100°	2.9	0.7613	1.41790
120–130°	1.1	0.8123	1.45577
Residue	6.3	0.9387	1.54107

The fraction of b.p. 73–75° was confirmed to be mostly composed of methyl cyclopentane from the measurement of its physical constants. Higher boiling fractions were assumed, from their physical constants, to be composed of polymerized forms of cyclohexene.

When, however, 50 gr. of cyclohexane were treated under the same conditions as cyclohexene, no appreciable change took place, as will be shown in the results of fractionations of the product.

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(1) Tiffeneau, *Ann.*, **405** (1914), 129.
(2) Markonikoff, *Ber.*, **31** (1898). 1223.
(3) Zelinski, *Ber.*, **30** (1899), 388.

TABLE 6.

Fraction	Yield gr.	d_{20}^{20}
78-80°.7	32.7	0.7753
81-82°	6.2	0.7780
82-85°	8.9	0.7785

It is probable that hexamethylene, by the catalytic action of the Japanese acid earth, rearranges itself, at least in part, to form the more stable pentamethylene, even in case of these compounds in which one or more of the hydrogen atoms of the nucleus is replaced by a methyl group, or other long paraffine side-chains ; and it is reasonable to suppose that these compounds would react in a manner analogous to that of the mother alcohol itself, since methyl cyclohexanone and menthone behave in a similar way as cyclohexanone toward lead peroxide and sulphuric acid.(1)

To demonstrate the above speculation, methyl cyclohexanol (1 : 2) prepared from o-cresol by catalytic reduction with reduced nickel and hydrogen at 180° (b.p. 167–170° ; $d_{20}^{20}=0.9330$; $d_0^0=0.9473$; $n_D^{20}=1.45998$), was passed over the earth heated at 250° and 350° respectively, and the following results were obtained.

When 150 gr. of the alcohol treated at 250°, in presence of the catalyst, 94.0 gr. of oil, 21.3 gr. of water and some gaseous substance were obtained, and the former was divided into the following 11 portions after fractional distillation 10 times.

TABLE 7.

No.	Fraction	Yield gr.	d_0^0	d_{20}^{20}	d_0^{20}	n_α^{20}	n_D^{20}	n_γ^{20}	Methyl cyclohexene, % (by Br-value.)
1	to 86°	2.7	0.7948	0.7783	0.7771	1.42658	1.42940	1.44115	—
2	86–90°	2.9	0.7998	0.7846	0.7835	1.42940	1.43211	1.44331	—
3	90–95°	4.2	0.8018	0.7859	0.7847	1.43090	1.43362	1.44498	90.55
4	95–99°	7.7	0.8039	0.7877	0.7866	1.43242	1.43512	1.44675	95.49
5	99–102°	11.4	0.8047	0.7902	0.7891	1.43383	1.43652	1.44841	98.45
6	102–105°	13.4	0.8082	0.7925	0.7913	1.43565	1.43843	1.45059	99.33
7	105–110°	13.8	0.8135	0.7983	0.7974	1.43847	1.44125	1.45362	about. 100
8	110–115°	1.6	0.8228	0.8085	0.8074	1.44248	1.44451	—	—
9	115–120°	1.4	0.8279	0.8133	0.8121	1.44300	1.44597	—	—
10	120–170°	1.0	0.8645	0.8497	0.8485	1.44812	1.45092	—	—
11	Residue	16.2	—	—	—	—	—	—	—

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(1) O. Wallach, Mathilde Gerhardt and W. Jessen, *J. Chem. Soc.*, **110** (1916), 487.

The fraction of b.p. 90–95° was confirmed as composed of methyl cyclohexenes by its physical constants, elementary analysis (C=86.58; H=13.32%) and also by the bromine-test, and other fractions with b.p. from 95–99° to 105–110° were also ascertained, in a similar manner to that of the third fraction, to consist of methyl cyclohexenes.

The occurrence of methyl-cyclohexene in the fractions mentioned above, was demonstrated by transforming the hydrocarbons present in the fractions with b.p. 99–102° and 102–105° with conc. nitric acid into an acidic sudstance with a m.p. of 152–153°, which shows no lowering of its melting point when mixed with pure adipic acid.

When 150 gr. of the methyl-cyclohexanol were passed over the catalyst heated at 350°, 118.4 gr. of oil ($d_0^{20}=0.8174$; $n_D^{20}=1.46145$) and 26.5 gr. water were obtained, and the oily substance was treated, to isolate some derivatives of cyclopentane formed from methyl-cyclohexanol by contact action of the catalyst, with conc. sulphuric acid to remove the unsaturated hydrocarbons formed from the alcohol, from the saturated ones which occur in the oil. The saturated hydrocarbons which remained, escaped from the reaction of the conc. sulphuric acid, were composed of 25 gr. of a liquid whose boiling point was 80–120°, and 12.4 gr. of another one of higher boiling point. The latter was divided into two fractions by steam distillation, namely 6.4 gr. of volatile ($d_0^{20}=0.8806$) and 3.6 gr. of non-volatile part.

25 gr. of the fraction with b.p. 80–120° were fractionated 10 times, and were divided into the following 8 fractions, each fraction was studied for its density and for the index of refraction and the results are shown in Table 8.

TABLE 8.

No.	Fraction	Yield gr.	d	d_{20}^{20}	d_0^{20}	n_α^{20}	n_D^{20}	n_γ^{20}	Molecular dispersion
1	85–90°	1.7	0.7656	0.7498	0.7488	1.41050	1.41212	1.42163	—
2	90–92°	1.4	0.7716	0.7552	0.7541	1.41311	1.41515	1.42460	0.83
3	92–94°	1.3	0.7747	0.7589	0.7578	1.41482	1.41680	—	—
4	94–96°	2.4	0.7763	0.7612	0.7601	1.41592	1.41810	1.42763	—
5	96–98°	5.2	0.7789	0.7634	0.7623	1.41723	1.41940	1.42884	—
6	98–101°	7.7	0.7815	0.7665	0.7654	1.41833	1.42050	1.43008	0.78
7	101–104°	1.9	0.7850	0.7694	0.7683	1.42034	1.42250	—	—
8	Residue	0.9	—	—	—	—	—	—	—

As will be seen in the above table, the fraction of b.p. 90–92° was noticed to be composed of dimethyl cyclopentane from its physical constants (index of refraction, density and dispersion), and this was also confirmed by elementary analysis: C=85.12; H=15.02, C_7H_{14} requires C=85.71;

H=14.29%. Thus, the occurrence of dimethyl cyclopentane in the reaction product, due to the contact isomerisation of methyl cyclohexene, was demonstrated. The fraction with b.p. 98–101°, to our interest, was learned to be composed of methyl cyclohexane so far studied for its density, index of refraction and dispersion, and also for its elementary composition (C=85.53; H=14.62; C_7H_{14} requires C=85.71; H=14.29%). For identification, it was subjected to contact oxidation by passing it on reduced nickel heated at 350° and toluene was obtained. This hydrocarbon was regarded as originating the contact action of conc. sulphuric acid on methyl cyclohexene, which was used in the previous treatment to clear the unsaturated hydrocarbons from the saturated ones, since methyl cyclohexene, according to Maquenne's report,(1) was actually transformed by the contact action of the acid into methyl cyclohexane.

In order to get more precise knowledge of the formation of methyl cyclohexane from methyl cyclohexene during the treatment, and also the occurrence of its isomeric dimethyl cyclopentane and methyl cyclohexenes in the reaction product, 150 gr. of the alcohol were treated with the earth heated at 350°, in a similar manner as the previous example. 112.4 gr. of oily product (d_0^0=0.8363) were obtained, which was then subjected to fractional distillation 10 times without treatment with sulphuric acid and the following 11 portions were obtained.

TABLE 9.

No.	Fraction	Yield gr.	d_0^0	d_{20}^{20}	d_0^{20}	n_α^{20}	n_D^{20}	n_γ^{20}	Methyl cyclohexene % (by Br-value)
1	75-78°	2.7	0.7659	0.7489	0.7481	1.41352	1.41610	1.42656	—
2	78-82°	3.6	0.7792	0.7610	0.7602	1.41844	1.42095	—	—
3	82-89°	4.3	0.7847	0.7677	0.7669	1.42135	1.42390	1.43489	22.10
4	89-92°	5.2	0.7879	0.7720	0.7712	1.42401	1.42670	1.43734	—
5	92-95°	7.2	0.7930	0.7760	0.7753	1.42668	1.42930	—	—
6	95-99°	7.8	0.7961	0.7793	0.7784	1.42909	1.43191	1.44331	82.95
7	99-102°	16.1	0.8067	0.7901	0.7893	1.43585	1.43863	—	98.25
8	102-105°	14.6	0.8134	0.7976	0.7967	1.44109	1.44416	1.45716	99.87
9	105-110°	16.5	0.8224	0.8060	0.8051	1.44671	1.44987	1.46366	about 100
10	110-120°	2.0	0.8361	0.8191	0.8182	1.45463	1.45807	1.47274	—
11	Residue	21.6	—	—	—	—	—	—	—

The reaction product, from its physical constants, elementary analysis and also the bromine value measured following the directions of

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(1) Maquenne, *Bull. Soc. Chim.*, [3] 9 (1893), 129.

McIlhiney,(1) was considered to be composed of 20% dimethyl cyclopentane and 40% methyl cyclohexene. The fraction with b.p. 99–102°, after being confirmed to be composed of methyl cyclohexene but not cyclohexane, was subjected to oxidation with conc. nitric acid, and oxalic, succinic, adipic (this being the main product) and β-methyl adipic acids were isolated from the reaction product, and also were ascertained by the determination of the melting point.

From the above investigations, it is evident that methyl cyclohexanol, when heated at 250° in presence of the Japanese acid earth, yields methyl cyclohexene as main reaction product, while at 350° the reaction proceeded to form dimethyl cyclopentane from some part of the methyl cyclohexene, but the isomerisation of hexamethylene to pentamethylene hydrocarbon takes place usually under high pressure. Further course of the reaction involved is not clear, but the products are olefines of low molecular weight and polymers of the unsaturated hydrocarbons.

Thus, the contact isomerisation of hydrocarbons of the polymethylene series, besides promoting the actions of dehydration and polymerisation, was forced to denote a special feature of the contact actions of the Japanese acid earth.

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Hatagaya, Tokyo.

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(1) McIlhiney, *J. Soc. Chem. Ind.*, **13** (1894), 668.

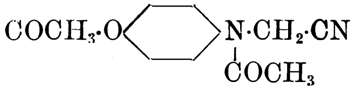
SOME DERIVATIVES OF HYDROXYPHENYLGLYCINE. II.

By **Kotaro SHIMO.**

Received July 29, 1926. Published October 28, 1926.

Acetyl or Benzoyl Derivatives of Hydroxyphenylglycine Nitriles.

1. **Diacetyl-p-hydroxyanilidoacetonitrile.**



7.4 Gr. of the nitrile were treated with 11.5 c.c. of acetic anhydride, in an alkaline solution, 8 gr. of diacetyl-p-hydroxyanilidoacetonitrile was obtained, which was recrystallised several times from 50% alcohol, in small white platy crystals melting at 94–95° (uncorr.). Galatis(2) described 75° for its

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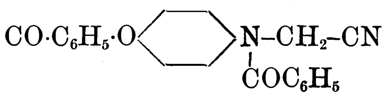
(2) See this journal 1 (1926), 202.

melting point. The analytical results and chemical properties of this substance agree with those described by Galatis.

0.1763 gr. subst. gave 0.4028 gr. CO_2 and 0.0807 gr. H_2O. 0.1888 gr. subst. gave 18.8 c.c. N_2 (9°, 765 mm.). (Found: C=62.31; H=5.09; N=12.47. $C_{12}H_{12}O_3N_2$ requires C=62.07; H=5.17; N=12.07%).

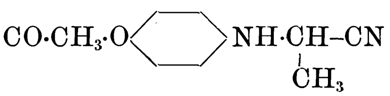
2. Dibenzoyl-p-hydroxyanilido-acetonitrile.



It was prepared by the action of benzoyl chloride on p-hydroxyanilido-acetonitrile in alkaline solution, and found to melt at 129–130° (uncorr.).

0.1092 gr. subst. gave 0.2980 gr. CO_2 and 0.0462 gr. H_2O. 0.0921 gr. subst. gave 6.3 c.c. N_2 (10.5°, 749.4 mm.). (Found: C=74.40; H=4.70; N=8.16. $C_{11}H_{12}O_3N_2$ requires C=74.16; H=4.49; N=7.87%).

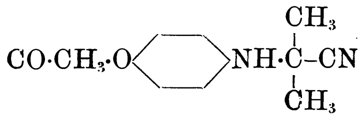
3. Acetyl-p-hydroxyanilidomethyl-acetonitrile.



The acetyl compound was obtained by acetylation of the nitrile by means of acetic anhydride and sodium acetate at room temperature. The pure substance was obtained as small platy crystals melting at 129–131° (uncorr.).

0.1136 gr. subst. gave 0.2683 gr. CO_2 and 0.0617 gr. H_2O. 0.1031 gr. subst. gave 12.2 c.c. N_2 (13°, 757.5 mm.). (Found: C=64.41; H=6.31; N=14.14. $C_{11}H_{12}O_2N_2$ requires C=64.71; H=5.88; N=13.73%).

4. Acetyl-p-hydroxyanilidodimethyl-acetonitrile.



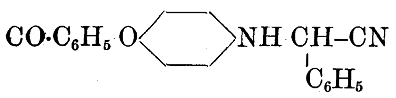
The nitrile was acetylated with acetic anhydride in alkaline solution and the crude product was purified from alcohol solution. The pure substance is beautiful long needles and melts at 77–78° (uncorr.).

0.1195 gr. subst. gave 0.2875 gr. CO_2 and 0.0712 gr. H_2O. 0.1059 gr. subst. gave 11.3 c.c. N_2 (9.5°, 764 mm.). (Found: C=65.61; H=6.67; N=13.02. $C_{12}H_{14}O_2N_2$ requires C=66.05; H=6.42; N=12.85%.)

The nitrile, however, on benzoylation by means of Schotten-Bauman's method instead of the expected benzoyl derivative, dibenzoyl-p-aminophenol, melting at 233–234° (uncorr.) was the result.

0.1121 gr. subst. gave 4.25 c.c. N_2 (11.5°, 761.5 mm.). (Found: N=4.58. $C_{20}H_{15}O_3N$ requires N=4.42%).

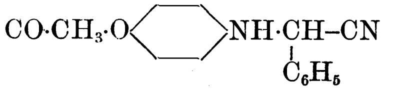
5. Benzoyl-p-hydroxyanilidophenylacetonitrile.



The nitrile was benzoylated by means of Schotten-Bauman's method and the benzoyl derivative which was recrystallised from alcohol, began to sinter at 160° and melted clear at about 200°.

0.1209 gr. subst. gave 0.3389 gr. CO_2 and 0.0537 gr. H_2O. 0.1336 gr. subst. gave 8.1 c.c. N_2 (13.5°, 762.6 mm.). (Found: C=76.63; H=4.97; N=8.95. $C_{21}H_{16}O_2N_2$ requires C=76.83; H=4.89; N=8.54%).

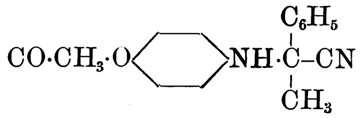
6. Acetyl-p-hydroxyanilidophenylacetonitrile.



The nitrile was acetylated by means of acetic anhydride, in alkaline solution, and the pure acetyl derivative melting at 119–120° was obtained as small hexagonal crystals.

0.1262 gr. subst. gave 0.3330 gr. CO_2 and 0.0601 gr. H_2O. 0.1067 gr. subst. gave 9.8 c.c. N_2 (9°, 758 mm.). (Found: C=71.97; H=5.29; N=11.14. $C_{16}H_{14}O_2N_2$ requires C=72.18; H=5.26; N=10.53%).

7. Acetyl-p-hydroxyanilidophenylmethylacetonitrile.



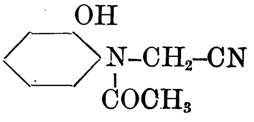
The acetyl compound was obtained by acetylation of the nitrile either by acetic anhydride in alkaline solution or by acetic anhydride and sodium acetate. It was purified by dilute alcohol and the pure substance melts at 142–143° (uncorr.).

0.1137 gr. subst. gave 0.3042 gr. CO_2 and 0.0587 gr. H_2O. 0.1059 gr. subst. gave 9.0 c.c. N_2 (8°, 759.4 mm.). (Found: C=72.97; H=5.78; N=10.36. $C_{17}H_{16}O_2N_2$ requires C=72.86; H=5.71; N=10.00%).

By the action of benzoyl chloride and alkali on the nitrile, dibenzoyl-p-aminophenol melting at 233–234° (uncorr.) was obtained.

0.1025 gr. subst. gave 0.2851 gr. CO_2 and 0.0452 gr. H_2O. (Found: C=75,86; H=4.90. $C_{20}H_{15}O_3N$ requires C=75.71; H=4.73%).

8. Acetyl-o-hydroxyanilidoacetonitrile.



When the crude nitrile which was extracted with ether from the reaction mixture, above mentioned,(1) was acetylated immediately by acetic anhydride, in alkaline solution, monoacetyl derivative was obtained. The pure sub-

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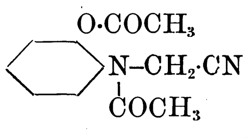
(1) This journal 1 (1926), 206.

stance which was purified from alcohol solution is fine colorless cubic crystals melting at 167–168° (uncorr.). It shows a pale reddish violet coloration with ferric chloride, yellowish red coloration with conc. nitric acid and red coloration with Millon's reagent.

0.1249 gr. subst. gave 0.2893 gr. CO_2 and 0.0606 gr. H_2O. 0.1064 gr. subst. gave 13.25 c.c. N_2 (10°, 757 mm.). (Found: C=63.17; H=5.39; N=15.03. $C_{10}H_{10}N_2O_2$ requires C=63.30; H=5.26; N=14.74%).

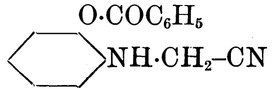
9. Diacetyl-o-hydroxyanilidoacetonitrile.



When the pure nitrile was acetylated with acetic anhydride and sodium acetate at room temperature, the diacetyl cempound was obtained. It consists of colorless needles which melt at 105–106° (uncorr.).

0.1203 gr. subst. gave 0.2715 gr. CO_2 and 0.0603 gr. H_2O. 0.1055 gr. subst. gave 10.8 c.c. N_2 (9.5°, 753.4 mm.). (Found; C=61.55; H=5.57; N=12.37. $C_{12}H_{12}O_3N_2$ raquires C=62.07; H=5.17; N=12.07%).

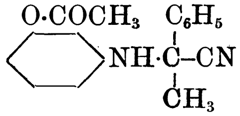
10. Benzoyl-o-hydroxyanilidoacetonitrile.



The nitrile was benzoylated by Schotten-Bauman's method. The benzoyl-o-hydroxyanilidoacetonitrile was obtained as fine white crystalline powder melting at 120–121° (uncorr.).

0.1121 gr. subst. gave 0.2942 gr. CO_2 and 0.0504 gr. H_2O. 0.1337 gr. subst. gave 12.7 c.c. N_2 (13°, 755.8 mm.). (Found: C=71.56; H=5.00; N=11.33. $C_{16}H_{12}O_2N_2$ requires C=71.43; H=4.76; N=11.11%).

11. Acetyl-m-hydroxyanilidophenylmethylacetonitrile.

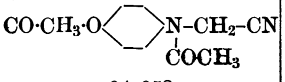
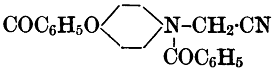
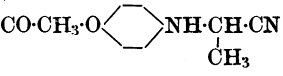
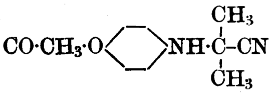
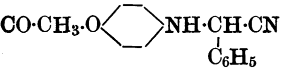
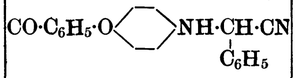
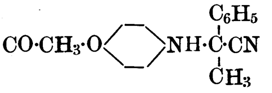
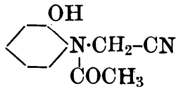
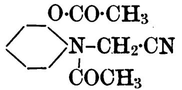
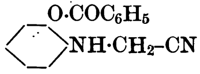
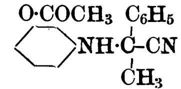


When the nitrile was acetylated by acetic anhydride and sodium acetate, the acetyl compound was obtained which was purified by dilute alcohol. It melts at 123–124° (uncorr.).

0.1199 gr. subst. gave 0.3182 gr. CO_2 and 0.0630 gr. H_2O. 0.1059 gr. subst. gave 8.9 c.c. N_2 (11°, 766.5 mm.). (Found: C=72.38; H=5.88; N=10.42. $C_{17}H_{16}O_2N_2$ requires C=72.86; H=5.71; N=10.00%).

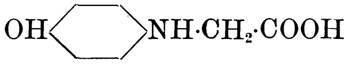
The solubilities of the acetyl or benzoyl derivatives of hydroxyphenylglycinenitriles in organic solvents and also in acids or alkalies are mentioned in Table 1.

TABLE 1.

Substance.	Acetone, alcohol, acetic ester, or glac. acetic acid.	Benzene, ether or chloroform.	Ligroin or water.	Caustic alkalies or mineral acids.
 $CO\cdot CH_3\cdot O\langle\;\rangle\underset{COCH_3}{N}\text{-}CH_2\text{-}CN$ m.p. 94–95°	soluble.	soluble. spar. sol. in ether.	sol. in hot water.	insoluble.
 $COC_6H_5O\langle\;\rangle\underset{COC_6H_5}{N}\text{-}CH_2\cdot CN$ m.p. 129–130°	soluble.	soluble.	insoluble.	insoluble.
 $CO\cdot CH_3\cdot O\langle\;\rangle NH\cdot\underset{CH_3}{CH}\cdot CN$ m p. 129–131°	soluble.	soluble.	spar. soluble.	sol. in acid. insol. in alkali.
 $CO\cdot CH_3\cdot O\langle\;\rangle NH\cdot\overset{CH_3}{\underset{CH_3}{C}}\text{-}CN$ m.p. 77–78°	soluble.	soluble.	insoluble.	sol. in acid. insol. in alkali.
 $CO\cdot CH_3\cdot O\langle\;\rangle NH\cdot\underset{C_6H_5}{CH}\cdot CN$ m.p. 119–120°	soluble.	soluble.	insoluble.	insoluble.
 $CO\cdot C_6H_5\cdot O\langle\;\rangle NH\cdot\underset{C_6H_5}{CH}\cdot CN$ m.p. 200°	soluble.	soluble. spar. sol. in ether.	insoluble.	insoluble.
 $CO\cdot CH_3\cdot O\langle\;\rangle NH\cdot\overset{C_6H_5}{\underset{CH_3}{C}}\cdot CN$ m.p. 142–143°	soluble.	soluble.	insoluble.	insoluble.
 $\overset{OH}{\langle\;\rangle}\underset{COCH_3}{N}\cdot CH_2\text{-}CN$ m.p. 167–168°	soluble.	spar. sol.	spar. sol. in water.	soluble in alkali. insol. in acid.
 $\overset{O\cdot CO\cdot CH_3}{\langle\;\rangle}\underset{COCH_3}{N}\text{-}CH_2\cdot CN$ m.p. 105–106°	soluble.	soluble.	spar. sol.	insoluble.
 $\overset{O\cdot COC_6H_5}{\langle\;\rangle}NH\cdot CH_2\text{-}CN$ m.p. 120–121°	soluble.	spar. sol. sol. in chloroform.	insol. in water.	sol.in conc. HCl. insol. in alkali.
 $\overset{O\cdot COCH_3}{\langle\;\rangle}NH\cdot\overset{C_6H_5}{\underset{CH_3}{C}}\text{-}CN$ m.p. 123–124°	soluble.	soluble.	insoluble.	insoluble.

Derivatives of Hydrophenylglycine.

1. p-Hydroxyanilidoacetic Acid.
(p-Hydroxyphenylglycine.)



This substance was obtained from p-hydroxyanilidoacetonitrile by saponifying with dilute caustic soda in 84.2% yield of the theory.

0.1822 gr. subst. gave 0.3823 gr. CO_2 and 0.0885 gr. H_2O. 0.1537 gr. subst. gave 10.7 c.c. N_2 (10°, 764 mm.). (Found: C=57.28; H=5.40; N=8.48. $C_8H_9O_3N$ requires C=57.49; H=5.39; N=8.38%).

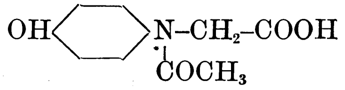
2. Ethyl and Methyl Ester of p-Hydroxyanilidoacetic Acid.

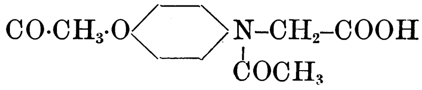
p-Hydroxyanilidoacetic acid yield the ethyl and methyl ester when dry hydrogen chloride gas was passed into the corresponding alcoholic solution of the acid, and then neutralising hydrochloride of the ester with sodium carbonate solution. The ethyl ester, thus obtained, was white leaflets, melting at 78–79° (uncorr.) and methyl ester at 97–98° (uncorr.).

0.1663 gr. of the ethyl ester gave 0.3748 gr. CO_2 and 0.0989 gr. H_2O. 0.1932 gr. of the subst. gave 12.25 c.c. N_2 (19°, 751.4 mm.). (Found: C=61.47; H=6.61; N=7.36. $C_{10}H_{13}O_3N$ requires C=61.54; H=6.67: N=7.18%).

0.1695 gr. of the methyl ester gave 0.3696 gr. CO_2 and 0.0910 gr. H_2O. 0.1562 gr. of the subst. gave 10.6 c.c. N_2 (20°, 753 mm.). (Found: C=59.47; H=5.97; N=7.87. $C_9H_{11}O_3N$ requires C=59.67; H=6.08; N=7.74%).

3. Mono-and Di-acetyl-p-hydroxyanilidoacetic Acid.

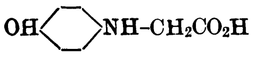
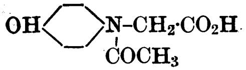
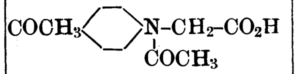
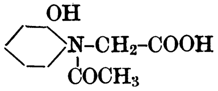




When p-hydroxyanilidoacetic acid is treated with acetic anhydride in alkaline solution, it yields diacetyl-p-hydroxyanilidoacetic acid which melts at 174–175° (uncorr.). When, however, ethereal solution of acetic anhydride is used as an acetylation agent monoacetyl derivative is formed, which crystallizes from hot aqueous solution in white prisms, melting at 203–204° (uncorr.).

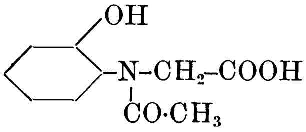
0.1566 gr. of the diacetyl subst. gave 0.3263 gr. CO_2 and 0.0736 gr. H_2O. 0.1728 gr. of the subst. gave 8.6 c.c. N_2 (18°, 753.5 mm.). (Found: C=56.81; H=5.22; N=5.82. $C_{12}H_{13}O_5N$ requires C=57.37; H=5.18; N=5.58%).

TABLE 2.

Substance.	Solubility.			Color Reaction.		
	Acetone, alcohol, ether, chloroform, acetic ester, benzene, or glac. acetic acid.	Water.	Caustic alkalies or mineral acids.	Ferric chloride.	Silver nitrate.	Am. silver nitrate.
	sparingly soluble.	spar. sol.	soluble.	violet-red.	greyish black ppt.	pale brownish yellow → blue colloidal.
 m.p. 78–79°  m.p. 97–98°	soluble.	sol. in hot. spar. sol. in cold.	soluble.	reddish violet.	pale reddish violet producing white ppt.	yellowish green colloidal → dirty green → greyish black ppt.
 m.p. 203–204°	sparingly soluble. sol. in alcohol or acetone.	sol. in hot. spar. sol. in cold.	soluble in alkali.	pale dirty violet.		
 m.p. 174–175°	soluble. spar. sol. in ether or benzene.	sol. in hot. spar. sol. in cold.	soluble in alkali.			
 m.p. 201–202°	soluble. spar. sol. in ether, chloroform or benzene.	spar. sol.	soluble in alkali. insoluble in acid.	pale reddish violet.		

0.1844 gr. of the monoacetyl subst. gave 0.3868 gr. CO_2 and 0.0857 gr. H_2O. 0.1721 gr. of the subst. gave 10.1 c.c. N_2 (18.5°, 753.9 mm.). (Found ; C=57.21; H=5.16 : N=6.85. $C_{10}H_{11}O_4N$ requires C=57.41 ; H=5.26 ; N=6.70%).

4. Acetyl-o-hydroxyanilidoacetic Acid (Acetyl-o-hydroxyphenylglycine).



Acetyl-o-hydroxyanilidoacetonitrile was boiled with dilute caustic soda until the evolution of ammonia had ceased, and then the solution was acidified with hydrochloric acid, whereby slightly brown-coloured sandy crystals were deposited.

Acetyl-o-hydroxyphenylglycine recrystallised from boiling water is colourless monoclinic crystals and melt at 201–202° (uncorr.) with slight decomposition.

0.1112 gr. subst. gave 0.2324 gr. CO_2 and 0.0537 gr. H_2O. 0.1267 gr. subst. gave 7.5 c.c. N_2 (13°, 755.5 mm.). (Found: C=57.00 ; H=5.40; N=7.08. $C_{10}H_{11}O_4N$ requires C=57.41 ; H=5.36 ; N=6.70%).

The solubility and the colour reactions of the derivatives of hydroxyphenylglycine are mentioned in Table 2.

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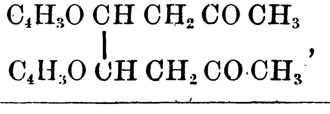
ÉTUDES DE DÉRIVÉS DU FURFURAL.
III. SUR LA TEINTE EN PASSAGE DES CÉTONES FURYLIQUES.

Par Itizo KASIWAGI.

Reçu le 21 août 1926. Publié le 28 octobre 1926.

On a déjà observé que les solutions des cétones furyliques se colorent sous l'action des alcalis caustiques du rouge clair au rouge brunâtre.(1) Ce sont les cétones furyliques avec les chaînes latérales *saturées* comme

furylbutanone	$C_4H_3O\cdot CH_2\,CH_2\,CO\cdot CH_3$,
furylpentanone	$C_4H_3O\,CH_2\,CH_2\,CO\cdot CH_2\cdot CH_3$,
difuryloctadione.	 $\begin{array}{l} C_4H_3O\,CH\,CH_2\,CO\,CH_3 \\ \quad\quad\quad\;\, \vert \\ C_4H_3O\,CH\,CH_2\,CO\,CH_3 \end{array}$,

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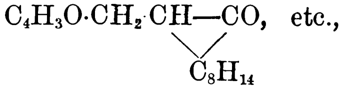
(1) I. Kasiwagi, ce journal, **1** (1926), 145.

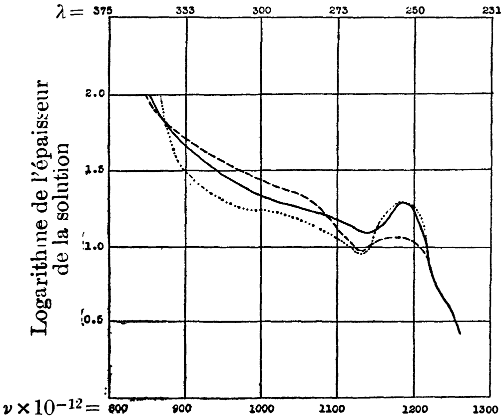
furfurylcamphre



$C_4H_3O{\cdot}CH_2{\cdot}\underset{C_8H_{14}}{CH{-}CO}$, etc.,

qui présentent ce phénomène.

Pour étudier cette coloration, nous avons pris tout d'abord les photographies de spectres d'absorptions. Dans ce but on a distillé les cétones mentionnées, on a préparé les solutions alcooliques à 1/100 N ajoutées avec l'éthylate de sodium en quantité équivalente, et il en a été résulté des solutions tout à fait incolores. Nous avons pensé que les solutions étaient trop étendues. Puis, en comparant les courbes de spectres d'absorptions des cétones seules avec celles des cétones en présence de l'alcali, on a trouvé qui les unes et les autres sont presque identiques (Fig. 1 et 2), c'est-à-dire que les cétones semblent ne subir aucune réaction en présence de l'alcali.

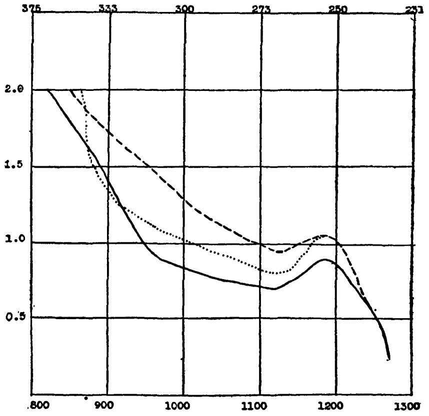


——— Furylbutanone antérieurement distillée; solution alcoolique à 1/100 N en présence de l'éthylate de sodium en quantité équivalente.

- - - - Furylbutanone à la même condition, mais freîchement distillée.

········ Furylbutanone seule, en solution alcoolique à 1/100 N.

Fig. 1.



——— Furylpentanone antérieurement distillée; solution alcoolique à 1/100 N en présence de l'éthylate de sodium en quantité équivalente.

- - - - Furylpentanone à la même condition, mais freîchement distillée.

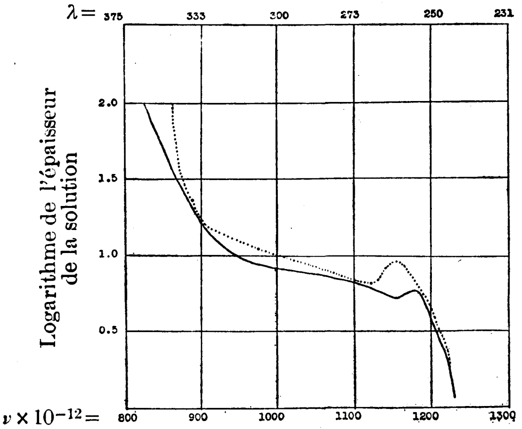
········ Furylpentanone seule, en solution alcoolique à 1/100 N.

Fig. 2.

Lorsque nous avons préparé le furylcamphre, nous avons éssayé si ce corps donne la même coloration avec l'alcali, et nous avons trouvé qu'il ne la donne pas *au moins* aux yeux. Les autres produits des cétones en solutions alcooliques se colorent en rouge en présence de l'alcali, comme les alcalis caustiques, les carbonates d'alcalis, l'ammoniaque, l'éthylate de sodium, etc. Les solutions rouges passent à leur tour au jaune après quelques heures.

Les résultats expérimentaux nous ont permis de tirer la conclusion que la coloration est attribuable à l'existence de composés inconnus formés soit par condensation soit par polymérisation des cétones, ayant absorbé les rayons ultraviolets, car il semble que cette formation des composés marche avec une certaine vitesse, et les cètones étudiées possèdent sans exception les bands d'absorptions dans cette région.(1)

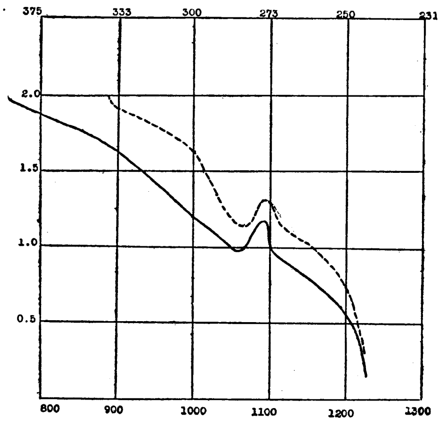
La tendance de se polymériser ou s'assodier du furfural et de ses dérivés a fait l'objet de nombreuses études. Getman a étudié l'association du furfural par voie cryoscopique, et il a constaté l'existence des molécules plus ou moins associées.(2) Toutes ces activités chimiques sont, de l'avis de ce savant américain,(3) dues à l'absorption des rayons dans la région ultraviolette, et naturellement le noyau furanique joue le rôle principal.



——— Furfurylcamphre; solution alcoolique à 1/100 N en présence de l'éthylate de sodium en quantité équivalente.

········· Furfurylcamphre seul en solution alcoolique à 1/100 N.

Fig. 3.



——— Difuryloctadione ; solution alcoolique à 1/100 N en présence de l'éthylate de sodium.

- - - - Difuryloctadione seule; en solution alcoolique à 1/100 N.

Fig. 4.

Partie expérimentale.

1er éssai : Les solutions alcooliques des cétones citées ci-dessus donnent sans exception la coloration rouge avec l'alcali, au bout d'un certain temps, un jour environ, après la purification, soit par distillation soit par cristallisation.

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(1) I. Kasiwagi, ibid., **1** (1926), 147.

(2) Getman, *J. Phys. Chem.*, **29** (1925), 395.

(3) Getman, ibid., **28** (1924), 397.

Au contraire les solutions ne donnent pas la coloration, quand on dissout les cétones tout de suite après la purification.

2ème essai : Les cétones, ainsi que les résidus de distillation de ces corps, se colorent en solutions alcooliques avec les alcalis. Les salutions rougies passent au jaune clair après une dizaine d'heures.

3ème essai : Les solutions alcooliques sans couleur se teignent en brun ou rouge brunâtre après plusieurs heures, tandis que les solutions aqueuses ou suspensions dans l'eau (également incolores quand les cétones sont fraîchement distillées) ne se colorent pas. Seulement après une demidouzaine de jours celles-ci colorent faiblement en jaune, bien que la solubilité soit apparemment beaucoup moindre en eau qu'en alcool.

4ème essai : Les solutions rouges passent au jaune claire, quand on les chauffe. Les solutions rougies par l'ammoniaque jaunissent pareillement par l'addition de l'acide, et elles ne rougissent jamais, étant rendues alcalines par l'ammoniaque et, au contraire, elles passent au jaune plus foncé. Ces réactions—les changements de couleurs—semblent irréversibles.

5ème essai : Études spectrographiques. Sur le dispositif spectrographique voir le deuxième mémoire.(1)

On voit plus ou moins la proportionnalité des déplacements des courbes d'absorptions avec la durée de la distillation des corps étudies jusqu'à la dissolution. Les courbes d'absorptions de la difuryloctadione en sont un bon exemple, car elles sont presque identiques sauf que l'une de la solution en prèsense de l'alcali indique l'absorption plus profonde vers le spectre visible. Cette dione que nous nous sommes servie fond à 119.5–120°.

Ces observations spectrographiques coincident très bien avec les éssais cités, et tous ces résultats expérimentaux nous permettent de conclure la formation des composés intermédiaires qui donnent cette coloration caractéristique avec l'alcali, et aussi que ces composés sont assez labiles.

Haute école polytechnique de Yokohama.

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(1) I. Kasiwagi, loc. cit.

LEPIDOLITE FROM NAGATORI, CHIKUZEN PROVINCE, AND THE LITHIUM CONTENT OF JAPANESE MICA.

By **Satoyasu IIMORI** and **Jun YOSHIMURA.**

Received September 11, 1926. Published November 28, 1926.

Abundant tiny scaly flakes of silvery white mica of pink shade occuring intimately associated with granular quartz of faint purple or pink colour has been formerly found to be lepidolite at the Nagatori district, prov. Chikuzen, Japan. No chemical investigation having been made before, so the authors has newly determined its constituents. It was, however, not able to obtain material entirely free from the quartz grains, and a portion of the associated mass which contained comparatively small amount of quartz was therefore taken for analysis. It gave the result of the second column in the table below. Now, leaving silica, which was due to the quartz admixed as gangue, out of account the result was recalculated to 100 per cent and the result is given in the third column of the table, showing the true composition of the lepidolite.

TABLE 1.

	(I)	(II)
SiO_2	56.79%	48.59%
Al_2O_3	21.71	26.33
Fe_2O_3	0.73	0.88
FeO	0.14	0.17
MnO	0.46	0.56
CaO	0.26	0.31
MgO	0.13	0.16
K_2O	6.23	7.56
Rb_2O	0.96	1.16
Na_2O	2.45	2.97
Li_2O	1.94	2.35
F	4.69	5.69
H_2O	4.67	5.66
	101.16	102.39
$\frac{1}{2}$ O (equiv. to F)	−1.97	−2.39
Total	99.19	100.00

In the above calculation, the amount of the quartz gangue was so deduced that the atomic ratio of silicon to alkali metals except lithium in lepidolite is generally 3, according to the recent views of A. N. Winchell(1) and A. F. Hallimond.(2) The analyzed mass consisted of about 17% quartz and 83% lepidolite of the composition above indicated. This ratio of lepidolite to quartz matrix in the congregated mass may of course widely vary.

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(1) *Am. Jour. Sci.*, **209** (1925), 415.

(2) *Mineralog. Mag.*, **20** (1925), 314.

Next, the content of lithia as well as potassia and sodia in a number of micas found in Japan was determined. The results obtained are given in Table 2.

TABLE 2.

Sample	Locality	Appearance	Alkalis determined			The atomic ratio: ($^{Li}/_{(Na+K)}$)
			Li_2O(%)	Na_2O(%)	K_2O(%)	
Lepidolite	Nagatori.	Small opaque scales of light grains rose colour, associated with quartz · · · ·	2.49	3.20	9.13	0.56
			1.94	2.70	6.71	0.59
			2.09	2.78	6.28	0.61
Zinnwaldites	Naegi.	Large transp. cryst. of light brown colour.	2.31	5.82	8.35	0.43
	Tanokami.	„ „ „ of light purple colour.	4.24	5.00	7.89	0.86
		„ „ „ of light brown colour	3.66	2.18	7.52	1.11
			2.44	3.54	10.74	0.48
Biotites	Ishigure	Large opaque cryst. of black colour · · ·	0.66	2.22	5.08	0.25
	Tanokami	„ „ „ „ „ „ · · ·	0.35	0.69	6.72	0.14
		Small „ „ „ „ „ · · ·	1.20	2.29	6.12	0.39
	Mategata.	Large „ „ „ „ „ · · ·	0.23	1.62	8.02	0.07
	Hajikano.	Small „ „ „ brown „ · · ·	0.29	1.95	4.57	0.17
	Sanpeyama	Small opaque scales of brown „ · · ·	0.09	3.42	3.99	0.03
Muscovites	Ishigure.	Small opaque scales of silvery white colour.	0.32	0.95	10.03	0.08
	Tanokami.	Large transp. cryst. · · · · · · · · · · ·	0.31	4.10	12.56	0.05
		Large opaque cryst. of silvery white. · · ·	0.17	2.74	10.92	0.04
		„ „ „ „ „ „ · · ·	1.41	1.15	11.60	0.34
	Otsukawa.	Small „ „ „ „ „ · · ·	0.26	2.20	8.44	0.07
Phlogopite	Kankyo.	Large transp. cryst. of dark green shade ·	0.22	2.47	10.30	0.07

It was found that some of the biotites showed fairly high content of lithium. Attention must, however, be called to the constant presence of lithia in all of the specimens analyzed, and it may be mentioned that the lithium is to be one of the common constituents of the mica.

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Hongo, Tokyo.

ALKALI METALS IN BERYL FROM ISHIKAWA, IWAKI PROVINCE.

By **Jun YOSHIMURA.**

Received September 11, 1926. Published November 28, 1926.

The alkali metals present in the beryl from Ishikawa were determined. The method of separation employed was the same as that used by Dr. S. Iimori and the author for the separation of rare alkalis in the Japanese lepidolite and zinnwaldite.(1) In the present case, however, caesium was precipitated as caesium stannic chloride and subsequently the weighed caesium sulphate obtained was spectrographically examined, especially for rubidium. But it was confirmed that the sulphate contained no rubidium. The analysis gave the following result:

Cs_2O	Li_2O	K_2O	Na_2O	Total alkalis
0.085%	0.015%	0.24%	0.49%	0.83%

These alkalis weighed as sulphate were all examined spectrographically and proved of their high purity.

The author wishes to thank Dr. S. Iimori for his kind advices.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.

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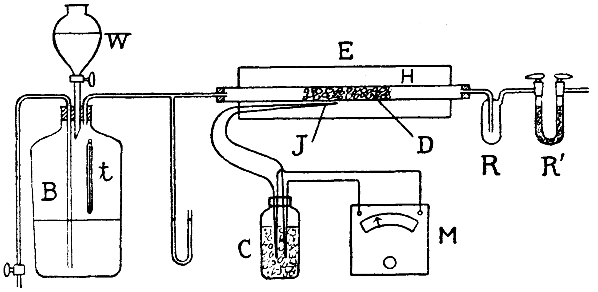
(1) This journal, **1** (1926), 215.

STUDIES ON THE PROPERTIES OF DIASPORE(1) AND BAUXITE.

By Yohei YAMAGUCHI and Toshimasa TAKEBE.

Received September 22, 1926. Published November 28, 1926.

Both of the minerals, diaspore and bauxite, can be decomposed to alumina and water by heating. But no investigation regarding vapour pressures of decomposition at various temperatures and heats of decomposition as well has yet been made. In order to determine the vapour pressures of decomposition of these minerals, the following experiments were carried out by employing an apparatus based on the dynamical method.



W: funnel
B: bottle of large capacity
t: thermometer
E: electric furnace
H: hard glass tube
D: powdered diaspore
J: thermo-junction
C: cold junction
M: millivoltmeter
R: receiver
R′: $CaCl_2$ tube

Fig. 1.

As soon as the temperature of the powdered diaspore or bauxite which have been packed in the tube H becomes constant (T in absolute scale), two receivers R and R′ are attached to the one end of the tube H and a certain quantity of water is allowed to drop down from the funnel W into the bottle B in such a slow velocity that the air replaced by the dropping water flows out, practically maintaining the equilibrium with the powdered material. After a definite quantity of water (v c.c.) was dropped, the water collected in R and R′ is weighed (g gr.). Room temperature (t°C) and barometric pressure (P mm. Hg.) are also observed. Then the vapour pressure of decomposition (π in mm. Hg.) at T can easily be calculated from these observed values.

The volume in c.c. of dry air passed at the temperature t°C. and under P mm. pressure is expressed by $\frac{(P-p)v}{P}$, where p denotes the vapour tension of water at t°C. If n be the number of gram molecules of g gr. of water

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(1) The more detailed report is found in *Bulletin of the Institute of Physical and Chemical Research* (in Japanese), 5 (1926), 17.

and w the volume of g gr. of water vapour at $t°$ and under P mm. pressure, then

$$n=\frac{g}{18.016}\quad\cdots\cdots(1)$$

and

$$Pw=nR(273+t)\quad\cdots\cdots(2)$$

Hence

$$w=\frac{gR(273+t)}{18.016\,P}\quad\cdots\cdots(3)$$

The total volume V is equal to, at $t°$ and under P mm., the sum of the volume of the dry air passed and that of the water vapour, thus

$$V=\frac{(P-p)v}{P}+w\quad\cdots\cdots(4)$$

And there is the relation $\frac{\pi}{760}=\frac{w}{V}$ $\cdots\cdots(5)$

So we have

$$\pi=\frac{760\,w}{\frac{(P-p)v}{P}+w}=\frac{760\times 3464\,g(273+t)}{(P-p)v+3464\,g(273+t)}\quad\cdots\cdots(6)$$

where 3464 is the numerical value of the constant R/18.016. As P, t, v and g are experimentally measurable values and p can be known from some table, the value of vapour pressure (π) at T can be calculated by equation (6).

Materials. The composition of diaspore used for the experiments⁽¹⁾ is expressed as $AlO(OH)$ from the result of X-ray analysis by J. Böhm.⁽²⁾ The formula of bauxite will be expressed as $Al_2O_3\cdot 2H_2O$ or $Al_2O(OH)_4$ as can be seen from Table 1, which has been obtained by authors.

TABLE 1.

Analysis of bauxite.

	SiO_2	Al_2O_3	Fe_2O_3	H_2O	Sum
Weight percentage.	5.4	62.0	10.7	22.0	100.1
Ratio of no. of gram mol.	1.335	9.06	1.00	18.2	

Decomposition Pressures of Diaspore and Bauxite. Experimental data and the calculated values therefrom of vapour pressures of diaspore and bauxite are shown in Tables 2 and 3.

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(1) The diaspore from Kanakura mine at Nagano province, Japan.

(2) J. Böhm, *Z. anorg. Chem.*, **149** (1925), 203.

TABLE 2. Diaspore.

Vol. of water dropped (v) c.c.	Barom. press. (P) mm. Hg.	Room temp. (t) °C.	Wt. of water collected (g) gr.	Vap. press. of diaspore at T (π) mm. Hg.	log π	Abs. temp. (T)	$1/T \times 10^6$
750	771	19.5	0.0211	27.7	1.436	698	1432
300	752	27	0.0330	103.0	2.0128	721	1387
750	771	19.5	0.0610	74.7	1.873	723	1383
3500	761	20	0.38	98.2	1.992	728	1374
500	770.7	19.5	0.1616	229.7	2.361	743	1346
1000	761	18.5	0.42	275.5	2.440	746	1341
500	770.7	19.5	0.3788	384	2.584	758	1320
250	752	27	0.2731	463	2.666	759	1317
200	752	27	0.5837	613	2.788	768	1301
200	752	27	0.9015	658	2.818	772	1295
180	761.3	19.5	1.31	690	2.839	773	1294
500	761	20	2.04	645	2.810	773	1294
——	760	——	——	760	2.881	775.5	1290

TABLE 3. Bauxite.

Vol. of water dropped (v) c.c.	Barom. press. (P) mm. Hg.	Room temp. (t) °C.	Wt. of water collected (g) gr.	Vap. press. of bauxite at T (π) mm. Hg.	log π	Abs. temp. (T)	$1/T \times 10^5$
700	758	21.5	0.1180	146	2.1644	503	199
300	765	20	0.0701	182	2.2601	517	194
400	746	27.5	0.1132	220	2.3421	526	190
400	746	27.5	0.1550	274	2.4378	546	183
300	753.5	29.2	0.1957	370	2.5682	548	182
200	761	18	0.5762	606	2.7825	570	175
450	755	21.5	0.9715	569	2.7551	573	174.5
300	746	27.5	0.6002	565	2.7520	577	173.5
200	760	22.5	0.3010	611	2.7860	581	172
300	755	21.5	2.0801	689	2.8382	598	167
200	746	27.5	1.5740	696	2.8426	604	165.5
300	753.5	29.2	2.2052	697	2.8432	606	165
300	754.5	27.5	0.1961	367	2.5647	628	159
300	746	28.8	0.1151	272	2.4346	631	158.5
200	756	27.0	0.0775	271	2.4330	648	154
200	754.5	27.5	0.2362	479	2.6803	655	153
300	746	28.8	0.1778	350	2.5441	656	152.5
200	756	27.0	0.2720	500	2.6990	677	148
200	746	28.8	0.2282	475	2.6767	690	145
200	754.5	27.5	0.3857	558	2.7466	690	145
200	756	27.0	0.3805	557	2.7459	701	143
200	754.5	27.5	0.1808	430	2.6336	720	139
200	756	27.0	0.2104	456	2.6590	723	138
200	746	28.8	0.2530	493	2.6928	730	137
200	756	27.0	0.4284	574	2.7589	756	132
200	746	28.8	0.4326	576	2.7604	791	126.5

In the case of diaspore, there exists a linear relation between log π and $1/T$ as shown in Fig. 2, and this agrees with the well known formula of Clapeyron and Clausius. From the curve of Fig. 2, the temperature at which the vapour pressure becomes 760 mm. is found to be 502.5°C. In the case of bauxite, there are found two distinct parts in the curve of $\log \pi$ and $1/T$ as shown in Fig. 3. The first part of the curve is straight while the second part is somewhat irregular. This requires a more precise experiment for it seems that this irregularity will be due to the slight deviation of equilibrium which may be occured between moist air and bauxite remained. It can hardly be considered that an impurities such as iron hydroxide give rise to such an irregularity, because the analysis of the bauxite shows that all of the water is exists in combination with alumina.

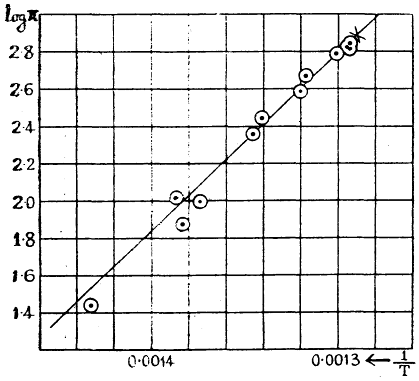

Fig. 2.

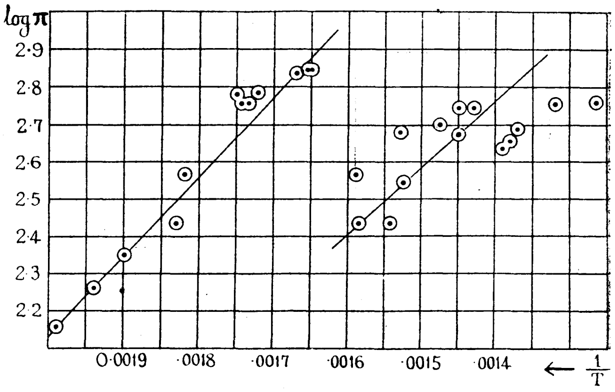

Fig. 3.

From this fact it may be concluded that the two parts of the curves came out from the decomposition of the hydrated alumina. The dehydrating decomposition in two stages was already found in some compounds having the water of crystallisation, but in hydroxide bauxite may be the first case ever known in such decomposition.

Heat of Decomposition. Diaspore and bauxite are decomposed by heating according to the following equations.

$$2AlO{\cdot}OH\ (\text{or } Al_2O_3{\cdot}H_2O) \longrightarrow Al_2O_3 + H_2O - Q$$
$$Al_2O\,(OH)_4\ (\text{or } Al_2O_3{\cdot}2H_2O) \longrightarrow Al_2O_2\,(OH)_2\ (\text{or } Al_2O_3{\cdot}H_2O) + H_2O - Q_1$$
$$Al_2O_2\,(OH)_2\ (\text{or } Al_2O_3{\cdot}H_2O) \longrightarrow Al_2O_3 + H_2O - Q_2$$

The values of the heat of decomposition in these cases (Q, Q_1 and Q_2) can be calculated by the following equation using two pairs of experimental data.

$$\log \frac{\pi_2}{\pi_1} = 0.4343 \frac{Q}{1.985} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

The calculated values are shown in Table 4.

TABLE 4.

	log π	$1/T$	Temp.	Heat of decomp.
Diaspore	2.8451 2.3671	0.001294 0.001346	500 470	Q = 42300 cal./mol.
Bauxite	2.8382 2.2601	0.001672 0.001934	325 244	Q_1 = 10100 „
Bauxite	2.6767 2.4346	0.001449 0.001585	417 358	Q_2 = 8100 „

Specific Heat of Diaspore. Specific heat of diaspore was determined by an ordinary calorimetric method. This value is necessary to calculate the total energy required to decompose the diaspore in ordinary temperature. It is found from the results of experiment that the mean specific heat of diaspore, in calories, is expressed by the following empirical equation in the range from 100°C to 400°C.

$$c = 0.2085 + 0.000127\,t.$$

Summary.

(1) It was found that the vapour pressures of decomposition of diaspore could be calculated by the following equation in the range from 400° to 500°.

$$\mathrm{Log}\,\pi = 14.820 - 9255.1/T.$$

(2) In the case of bauxite, the curve of decomposition pressure was found to be consisted of two parts. The first part can be expressed by the equation

$$\log \pi = 6.5277 - 2206.5/T,$$

in the range from 200° to 340°, and the second roughly by

$$\log \pi = 5.2566 - 1780/T$$

in the range from 350° to 450°.

(3) The heats of decomposition of diaspore and bauxite were calculated by the integrated equation of Clapeyron and Clausius.

(4) The specific heat of diaspore was determined by the calorimetric investigation and found to be

$$c = 0.2085 + 0.000127\,t.$$

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Hongo, Tokyo.

DIE LEITFÄHIGKEITSSTUDIEN DER ESSIGSÄURE IN AZETON.

Von **Naoyasu SATA.**

Eingegangen am 15, Oktober 1926. Ausgegeben am 28, November 1926.

Über die Anwendbarkeit in nichtwässriger Lösung des Ostwaldschen Verdünnungsgesetzes, nach welchem in wässriger Lösungen nur bei schwachen Elektrolyten bestätigt wurde, wurde es in letzter Zeit von mehreren Autoren wie P. Walden, H. Goldschmidt und andern studiert.(1)

Wenn man die Ergebnisse der genannten Untersuchungen überblickt, so fällt es einem auf, dass sie als Elektrolyte die sogenannten starken Elektrolyten angewandt wurden, so dass es mir sehr geeignet erscheint die Untersuchung über die Leitfähigkeit unter Anwendung der typischen schwachen Elektrolyt—Essigsäure—in Azeton als Lösungsmittel durchzuführen.

Für Leitfähigkeitsmessungen benutzte ich Widerstandskasten und als Tonquelle, Mitsubishische Wellenumformer. Das Leitfähigkeitsgefäss hat einen gut geschliffenen Glasstöpsel an welchem zwei Glasröhren geschmolzen sind, deren Spitzen senkrechte nicht-platinierte Platinblechelektroden trugen.(2)

Wegen der Schwierigkeiten der Reinigung und der Aufbewahrung des Lösungsmittels sowie der Lösungen, wurden die Messungen nach folgender zwei Richtungen ausgeführt.

(A) Nach Ostwaldsche Verdünnungsmethode.

(B) Zuerst füllt man das Gefäss mit reinem Lösungsmittel. Nach der Messung ihrer Eigenleitfähigkeit, tropft man den Elektrolyt ein und misst die Leitfähigkeit der Lösung. Die Konzentration derselben titriert man nachher mit einer N/100 Barythlösung.

Versuchsresultaten. I–Versuchsreihe: nach (A) Methode, bei 25° C. Versuch mit frischer molarer Lösung; als Lösungsmittel gebraucht man das nach der Destillation 5 Tage aufbewahrte Azeton.

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(1) P. Walden, "Elektrochemie nichtwässriger Lösungen", Leipzig, 1924.
R. Müller, "Elektrochemie der nichtwässrigen Lösungen," Stuttgart, 1923.
Godlewski, *J. chim. phys.*, **3** (1905), 393.
Fischler, *Z. Elektrochem.*, **19** (1913), 126.
Schreiner, *Z. physik. Chem.*, **111** (1924), 419.
Goldschmidt und Aas, *Z. physik. Chem.*, **112** (1924), 423.
Walden, Ulich und Laun, *Z. physik. Chem.*, **114** (1924), 275.
Ulich, *Z. physik. Chem.*, **115** (1925), 377; **117** (1925), 156.

(2) Dutoit et Levier, *J. Chim. phys.*, **3** (1905), 435.

$$\kappa_0 = 2.495 \times 10^{-7}$$

$v = 10^{-3}$	$\kappa_1 \times 10^7$	$(\kappa_1 - \kappa_0) \times 10^7 = \kappa \times 10^7$
16.19	20.94	18.45
32.38	12.41	9.92
64.76	8.14	5.65
129.52	5.86	3.37
259.04	4.599	2.10
518.08	3.85	1.35
1036.16	3.399	0.90

in dem : κ_0 = Eigenleitfähigkeit des Azeton,
κ_1 = Beobachtete Leitfähigkeit der Lösung,
v = Verdünnung in c.c. gezeignet.

II–Versuchsreihe : nach (A) Methode, bei 25° C. Versuch mit frischer molarer Lösung, zubereitet mittels frischem Azeton.

$$\kappa_0 = 0.644 \times 10^{-7}$$

$v = 10^{-3}$	$\kappa_1 \times 10^7$	$(\kappa_1 - \kappa_0) \times 10^7 = \kappa \times 10^7$
16.5	15.78	15.22
33.0	8.15	7.51
66.0	5.03	4.39
132.0	3.44	2.799
264.0	2.54	1.89
528.0	2.17	1.53
1056.0	1.95	1.31

III–Versuchsreihe : nach (B) Methode, bei 25° C.

$v = 10^{-3}$	$(\kappa_1 - \kappa_0) \times 10^7 = \kappa \times 10^7$	$v = 10^{-3}$	$(\kappa_1 - \kappa_0) \times 10^7 = \kappa \times 10^7$
10.25	13.81	224.1	1.55
17.48	18.19	284.8	1.899
11.07	12.29	299.5	1.76
18.00	9.94	334.1	1.22
29.55	8.32	415.9	1.25
30.85	7.36	448.1	1.12
44.19	6.34	462.4	0.91
63.45	4.56	494.1	0.97
88.25	3.04	516.1	0.97
99.21	3.18	608.5	0.66
129.9	1.88	614.9	0.73
144.5	2.52	722.6	0.43
155.4	2.74	802.9	0.90
175.9	2.08	825.1	0.63
200.2	1.32		

Erörterung. Das ganze Ergebnis der genannten Untersuchung wird graphisch in Fig. 1 dargestellt. Die Kurve in der Figur wird mit der Gleichung

$$K = \frac{\varkappa^2 v}{(I-\varkappa v)\, I}$$

gezeichnet, in welcher K und I zwei Konstanten sind und in diesem Falle die Werte,

$$K = 5.066 \times 10^{-6}$$
$$I = 0.06538$$

haben.

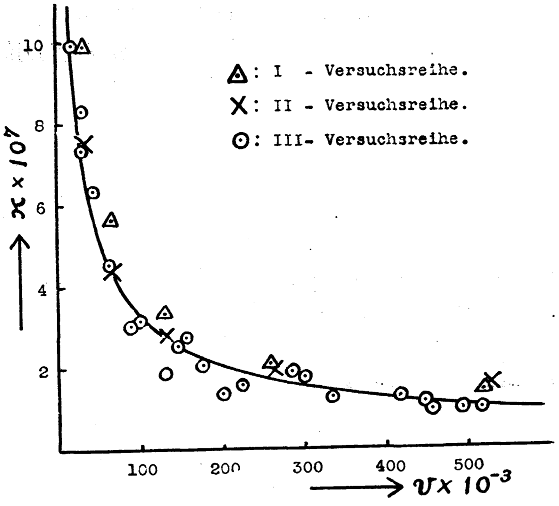

Fig. 1.

Es sei bemerkt, dass diese Gleichung dieselbe Form wie das Ostwaldsche Verdünnungsgesetz hat, wenn man

$\varkappa v = \mu_v$: Molekülare Leitvermögen betreffender Verdünnung v,

$I = \mu_\infty$: Molekülare Leitvermögen unendlicher Verdünnung setzt, worin das Verhältnis

$$\frac{\varkappa v}{I} = \frac{\mu_v}{\mu_\infty}$$

gewöhnlich als Dissoziationsgrad genannt ist. Also in diesem Versuchen hat dieses Verhältnis so grosser Wert wie z.B. bei $v = 500{,}000$, $\varkappa v/I = 0.77$. Da es nicht denkbar ist, dass das Dissoziationsgrad in der Wirklichkeit solche grossen Wert nehmen kann, so muss man annehmen, dass die undissozierte Moleküle auch die Elektrizität leiten, und deswegen kann das Verhältnis $\varkappa v/I$ nicht das sogenannte Dissoziationsgrad bezeichnen.

In dieser Studien übrigens stiess man an grossen Schwierigkeiten in der Reinigung des Lösungsmittels, sowie der Aufbewahrung der Lösungen und der Messung des grossen Widerstandes. Für weitere Studien der anderen schwachen Elektrolyten müssen wir mit besseren Einrichtungen uns vorsehen.

Zum Schluss erlaube ich mir meinen hochverehrter Lehrer Herrn Prof. J. Sameshima meinen aufrichtigsten Dank für seine stets liebenswürdige Leitung und Unterstützung.

Chemisches Institut, Kaiserliche Universität zu Tokyo.

LA DÉSHYDRATION DES ALCOOLS TERPÉNIQUES CYCLIQUES PAR LA TERRE ACIDE JAPONAISE.

(RECHERCHES SUR L'ESSENCE DE CAMPHRE VI)

Par **Kashichi ONO.**

Reçu le 6 octobre 1926. Publié le 28 novembre 1926.

J'ai montré anterieurement(1) que l'hydrate de terpine se transforme en para-cymène et en para-menthane par l'action catalytique de la terre acide Japonaise. Au cours de mes recherches ci-dessus sur l'hydrate de terpine, j'ai supposé que cet alcool aurait également donné d'abord en terpinéol et ensuite dipentène par déshydration de la terre acide Japonaise, mais je n'ai pu l'isoler.

Des présentes recherches ont été entreprises pour établir si les alcools terpéniques peuvent être déshydratés dans la phase liquide par l'action catalytique de la terre acide Japonaise, et pour confirmer si mon explication du mecanisme était correcte.

1° La terre acide Japonaise. C'est la terre de Fuller Japonaise ayant une poudre blanche un peu brunâtre et elle a la composition suivante :

Silice	63.71 %
Alumine	14.43 %
Oxyde ferrique	3.72 %
Chaux	1.33 %
Magnésie	1.63 %
Oxydes de potassium et de sodium	0.53 %
Perdu de calcination	14.97 %
	100.32

2° Hydrate de terpine. 200 gr. de l'hydrate de terpine est mélangé avec 20 gr. de la terre acide Japonaise(2) dans un ballon distillant avec un réfrigerant à reflux incliné. Le ballon est placé au bain d'huile et chauffé progressivement à presque 200°. On obtient, en distillant de l'eau et de la terpine par la déshydration. Après avoir chauffé presque 30 minutes une violente reaction se déclare, et le produit abondant se distille. La terre acide Japonaise se change en violet-brune. Les produits ainsi obtenus ont des propriétés suivantes :

	Rendement	d_4^{26}	n_D^{26}
L'huile distillée	66.6 gr.	0.8703	1.4710
Le résidu	53.1	0.9734	1.5014

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, 9 (1925), 153.

(2) La terre acide Japonaise a été desséchée à 100°.

En rectifiant sous 11.5–12 mm. de l'huile distillée, on obtient le fractions suivantes :

I	à 90°	22.9 gr.
II	90–95°	19.3 gr.
III	95–125°	8.1 gr.
IV	125–140°	1.9 gr.

Les fractions I (Eb. à 90°) et II (Eb. 90–95°) étaient redistillées sous pression ordinaire sur le sodium métallique.

			d^{28}_4	n^{28}_D
A	173–175°	3.2 gr.	0.8403	1.4660
B	175–176°	21.4	0.8418	1.4669
C	176–177°	6.7	0.8424	1.4688
D	177–180°	6.2	0.8456	1.4701

L'analyse de la seconde fraction (B) a donné les resultats suivants :

Analyse : 0.2109 gr. subst. donne 0.6798 gr. CO_2 et 0.2196 gr. H_2O. (Trouvé, C = 87.90 ; H = 11.69. Calculé pour $C_{10}H_{16}$, C = 88.15 ; H = 11.85 %.) Réfraction moléculaire : Trouvé, 44.55 ; Calculé pour $C_{10}H_{16}F_2$, 45.246.

On dissout 5.4 c.c. de la seconde fraction (B) dans 16.2 c.c. du mélange de poids égaux d'alcool amylique et d'éther et on y ajoute goutte à goutte 2.8 c.c. de brome dissous dans un mélange d'alcool amylique et d'éther, tout en refroidissant. Après avoir laissé reposer une nuit, sous l'addition de quelques gouttes de l'eau, on obtient les cristaux blancs. Ils se fondent à 124° après plusieurs récristallisations dans l'acétate d'éthyle. C'est le tétrabromure de dipentène qui est identique à celui décrit par les autres savants.

Les fractions III (Eb. 95–125°) et IV (Eb. 125–140°) ont été réfractionnées sous 11.5 mm., et ont donné :

46–95°	4.3 gr.
95–104°	0.5 gr.
104–107°	2.5 gr.
107–110°	1.3 gr.

Quand on traite la fraction bouillant vers 104–107° sous 11.5 mm. (d^{28}_4 = 0.9689, n^{29}_D = 1.4759) par l'isocyanate de phényl d'après O. Wallach⁽¹⁾, on obtient la phényluréthane en fines aiguilles, après récristallisation dans l'alcool, fondant à 112–113°. C'est la phényluréthane de α-terpinéol, qui était déjà obtenue par O. Wallach.⁽¹⁾

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(1) *Liebig's Ann. Chem.*, 275 (1893), 104.

En rectifiant le residu jaune claire avec la fluorescence verte, il passe en grande partie au-dessus de 300°. J'ai pensé que c'est le polymère comme le dipinène et le polyterpène, qui a été déjà signalé par Venable(1).

3° **Terpinéol liquide.** 50 gr. de terpinéol (Eb. 103–107° sous 12–14 mm.; $d_4^{20} = 0.9356$; $n_D^{21} = 1.4822$) est chauffé à 190–200° au bain d'huile avec 5 gr. de la terre acide Japonaise comme dans le cas précédent. Après avoir chauffé presque 20 minutes, il y a lieu une violente réaction et le produit abondant se distille. On obtient 21.7 gr. de l'huile distillée et 19.3 gr. de résidu dans le ballon distillant.

15 gr. de l'huile distillée a été redistillée sous pression ordinaire sur le sodium métallique.

I	170–175°	1.8 gr.
II	175–178°	7.6 gr.
III	178–180°	1.9 gr.
IV	180–185°	2.1 gr.

La fraction II (Eb. 175–178°) est redistillée encore sur le sodium métallique

169–175°	1.5 gr.
175–176°	3.9 gr.
176–180°	0.8 gr.

La fraction bouillant vers 175–176° présente les constantes suivantes :

$d_4^{29} = 0.8424$. $n_D^{29} = 1.4675$. Réfraction moléculaire : Trouvé, 44.864. Calculé pour $C_{10}H_{16}F_2$, 45.246.

Analyse : 0.1263 gr. subst. donne 0.4064 gr. CO_2 et 0.1321 gr. H_2O. (Trouvé, C = 87.75; H = 11.69. Calculé pour $C_{10}H_{16}$, C = 88.15; H = 11.85%).

En traitant cette fraction avec le brome, comme au précédent, on obtient le tétrabromure de dipentène fondant à 124°. J'ai donc pu constater que cette fraction bouillant vers 175–176° était le dipentène.

Le résidu a donné le même résultat comme le cas d'hydrate de terpine.

4° **l-Menthol.** 50 gr. de l-menthol fondant à 42–43°, $[\alpha]_D^{30} = -46.85°$ (en solution alcoolique) est traité à 180–195° au bain d'huile avec 5 gr. de la terre acide Japonaise. Après presque 20 minutes, il y a lieu une violente réaction et on obtient l'huile distillée ($d_4^{29} = 0.8098$, $n_D^{21} = 1.4481$) avec un rendement de 36.0 gr. et un peu de résidu.

30 gr. d'huile est distillée sur le sodium métallique et on obtient les fractions suivantes :

I	163–166°	0.3 gr.
II	166–168°	20.1 gr.
III	168–170°	6.0 gr.

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(1) *J. Am. Chem. Soc.*, 47 (1923), 730.

En rectifiant encore la fraction II bouillant vers 166–168° sur le sodium métallique, on isole la fraction bouillant vers 166–167.5° comme le produit principal et elle présente les constantes suivantes :

$d_4^{27} = 0.8062$. $n_D^{27} = 1.4470$. Réfraction moléculaire : Trouvé, 45.735, calculé pour $C_{10}H_{18}F_1$, 45.713. $[\alpha]_D^{29} = -3.26°$ (en solution alcoolique).

Analyse : 0.1385 gr. subst. donne 0.4397 gr. CO_2 et 0.1643 gr. H_2O. (Trouvé, C = 86.57 ; H = 13.26. Calculé pour $C_{10}H_{18}$, C = 86.87 ; H = 13.13%). Donc le corps obtenu est le l-menthène.

5° **d-Bornéol.** En chauffant 50 gr. de d-bornéol (F. à 203–204° ; $[\alpha]_D^{30} = +29.35°$ en solution alcoolique) pendant presque 30 minutes avec 5 gr. de la terre acide Japonaise au bain d'huile à 210–220°, on obtient 44 gr. de l'huile incolore et très peu de résidu. Dans ce cas je n'ai pu observer une violente réaction comme chacun de ces cas précédents.

30 gr. d'huile est redistillée cinq fois sur le sodium métallique et on obtient les fractions suivantes :

1^er. distillation.

à 155°	0.7 gr.
155–159°	0.8 gr.
159–163°	14.1 gr.
163–166°	6.4 gr.
166–170°	3.6 gr.
170–175°	1.3 gr.

5^me. distillation.

		d_4^{31}	n_D^{31}
152–158°	0.7 gr.	0.8482	1.4627
158–161°	15.5	0.8529	1.4638
161–163°	3.3	0.8537	1.4645
163–165°	2.0	0.8540	1.4659

La fraction bouillant vers 158–161° a donné à l'analyse les chiffres suivants :

Analyse : 0.1133 gr. subst. donne 0.3656 gr. CO_2 et 0.1196 gr. H_2O. (Trouvé, C = 87.99 ; H = 11.80. Calculé pour $C_{10}H_{16}$, C = 88.15 ; H = 11.85%). $[\alpha]_D^{31} = +23.76°$ (en solution alcoolique). Réfraction moléculaire : Trouvé 43.983, calculé pour $C_{10}H_{16}F_1$, 43.514.

J'ai pensé que cette fraction est un mélange d'un camphène cristallin et liquide. On a pu séparer les deux portions, la majeure partie du camphène cristallin et un peu de camphène liquide, par refroidissement dans la glace et le sel.

A. d-Camphène cristalline. Le cristal, qui se solidifie par refroidissement dans le glace et le sel, est séché sur une plaque poreuse et recristallisé deux fois dans l'alcool. Il fonde à 49.5° et présénte $[\alpha]_D^{28} = +31.10°$ (en solution alcoolique).

Analyse : 0.1075 gr. subst. donne 0.3478 gr. CO_2 et 0.1142 gr. H_2O. (Trouvé, C = 88.22; H = 11.87. Calculé pour $C_{10}H_{16}$, C = 88.15; H = 11.85%).

B. d-Camphène liquide. Après avoir séparé le camphène cristallin, on obtient un peu de camphéne liquide.

$d_4^{27} = 0.8598$ $n_D^{27} = 1.4672$ Réfraction moléculaire : Trouvé, 43.908, calc. pour $C_{10}H_{16}F_1$, 43.513. $[\alpha]_D^{28} = +11.12°$ (en solution alcoolique.)

Analyse : 0.1175 gr. subst. donne 0.3789 gr. CO_2 et 0.1224 gr. H_2O. (Trouvé, C = 87.93; H = 11.64. Calculé pour $C_{10}H_{16}$, C = 88.15; H = 11.85%).

Ce composé a déjà été obtenu par M. le Professeur Komatsu et son collaborateur(1) en deshydratant le d-bornéol en présence de thorine à 400° avec le gaz ammoniaque.

Laboratoire de Saiséi-Shono et Cie., Kobe.

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, 6 (1923), 65.

THE DETERMINATION OF THE HELIUM CONTENT OF SOME JAPANESE MINERALS.

By Jirô SASAKI.

Received November 2, 1926. Published December 28, 1926.

F. Bordas(1) has already noted the presence of helium in naegite, a radioactive mineral occurring in the Naegi district, Japan. No quantitative study on this line, however, having been made on the Japanese specimens of other minerals, so the author has undertaken the present investigation. That most minerals when simply heated evolve nearly half the amount of total helium contained, has been described by M. W. Travers,(2) and this method of extraction was adopted for the following helium determination.

The apparatus used was constructed according to the description of R. J. Strutt,(3) some parts of which were conveniently modified. A quantity of the powdered mineral was introduced in a quartzglass tube placed in an electric furnace, and heated in the exhausted state after having been washed with pure oxygen to remove all the air in the tube. The gas evolved was passed over solid potassium hydroxide, copper oxide heated to redness, and lastly over soda-lime, so as to remove most of hydrogen and carbon dioxide. The remaining gases were collected by a Toepler pump in an explosion eudiometer with platinum wires sealed in the top, and mixed with an excess of oxygen, the brush arc was then allowed to produce in the mixture by means of an induction coil to convert nitrogen into nitric oxide. The nitric acid thus formed was removed by the moistened fragments of solid potassium hydroxide floating on the surface of mercury in the eudiometer. After this operation was over, the excess of oxygen was absorbed by melted phosphorus. The gas, which was left unabsorbed and dried by phosphorus pentoxide, was introduced into a modified Geissler tube provided with electrodes of liquid alloy of potassium and sodium. Having been discharged between these electrodes, all traces of nitrogen, hydrogen, and carbon compounds were removed, and the remaining gas was finally subjected to the action of cocoanut charcoal chilled by liquid air. The gas thus having remained in apparatus was invariably pure helium which were always confirmed spectroscopically, and transferred into a narrow graduated burette where its volume was measured. The results are given in the following table.

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(1) *Compt. rend.*, **146** (1908), 628.

(2) *Proc. Roy. Soc.* (*London*), A, **64** (1898), 141.

(3) *Proc. Roy. Soc.* (*London*), A, **80** (1908), 572.

Mineral	Locality	Sample taken, gr.	Helium yielded, c.c. at N.T.P.	Helium c.c. per gr. of mineral	Helium %
Fergusonite	Naegi	10.03	1.16	0.12	0.0021
Monazite	Ishikawa	17.76	2.71	0.15	0.0027
Monazite sand	Sekigammen	60.95	9.53	0.16	0.0028
Monazite sand	Shokuzan	20.21	1.91	0.095	0.0017
Beryl	Ishikawa	40.93	0.10	0.0025	0.000044
Beryl	Tanokami	20.47	No He. was detected	—	—
Beryl	Naegi	20.82	No gas was evolved	—	—

According to Prof. Y. Shibata and K. Kimura,(1) monazite of Ishikawa contains 2.91 percent of ThO_2 and 0.85 percent of UO_3, while fergusonite of Naegi 11.08 percent of ThO_2 and 0.42 percent of UO_3. Using these data, the geological ages of both minerals were calculated after the method of E. Rutherford.(2) The volumes of helium, which are to be produced per year from each gram of these two minerals are 3.4×10^{-6} c.mm. and 1.57×10^{-6} c.mm. respectively. At these rates, the time required to produce twice the quantity of helium given in the above table is 90 million years for monazite and 150 million years for fergusonite. The comparatively lower values of helium content of those minerals may thus be ascribed to their younger geological ages.

In conclusion, the author wishes to express his sincere thanks to Dr. S. Iimori for his valuable suggestions and helpful advices while performing this work; his thanks are also due to Mr. S. Nishiyama for his assistances.

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(1) *J. Chem. Soc. Japan,* (in Japanese), 42 (1921), 1 & 957.

(2) " Radioactive Substances and Their Radiations," (1913) p. 562.

THE TRUE VISCOSITY AND THE COLLOIDAL VISCOSITY.

By Jitsusaburo SAMESHIMA.

Received November 12, 1926. Published December 28, 1926.

It is one of the characteristic properties of the lyophile sol that it has remarkably larger viscosity than that of the pure dispersing medium. Most of the organic " resinous " or " gelatinous " substances make viscous lyophile sols when they are brought into solutions. Cane sugar or glycerine, in the other hand, give viscous aqueous solutions though they are crystalline substances. The colloidal solutions are considered to be composed of very large " solute " particles suspended in the medium of solvent, so they may be called heterogeneous. In lyophile sols, moreover, these vulky particles have very porous structure. The viscosity of the lyophile sol is caused by the friction in moving of these vulky porous masses, or in other words friction in mass motion of solute and solvent molecules. But the viscosity of glycerine or cane sugar solution is caused by the friction between molecules of solvent or solute.

Now if we send a small particle—an ion—to travel through the liquid, then it will encounter some resistance. This resistance will be large if there are many obstacles—glycerin or sugar molecules—scattering in the way. And the resistance will be small if there are many channels of clear ways through which the particle can travel without being disturbed. The former case is assigned to the true or molecular viscosity and the latter to the colloidal viscosity. We may, therefore, clearly distinguish the two kinds of viscosities by the measurements of the electrical conductivities of the viscous solutions which contain a definite quantity of an electrolyte.

For the relation between the viscosity (η) and the conductivity, Johnstone(1) proposed the following equation,

$$\lambda = k\left(\frac{1}{\eta}\right)^m,$$

where λ is the equivalent conductivity of the solution, and k and m are constants for one kind of ion.(2) This equation may be applicable for the pure

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(1) Johnston, *J. Am. Chem. Soc.*, **31** (1909), 1010.

(2) Washburn, *J. Am. Chem. Soc.*, **33** (1911), 1461 & 1686.
Sachanov, *Z. Elektrochem.*, **19** (1913), 588.

aqueous solutions of salts, but cannot be used in our experiments, viz. alcohol, glycerine or sugar solutions. In the other hand Dumanski(1) has shown that the conductivity of the solution of an inorganic salt in gelatine jelly is only slightly less than those of equally concentrated solution in pure water.

Experimental. The apparatus used is shown in accompanying figure. This apparatus has been made by inserting two platinum electrodes in an Ostwald viscosimeter. So we can measure the viscosity and the conductivity of one liquid at the same time. The concentration of the solution was chosen so as its relative viscosity was 2.5 at 25°. This can easily be attained by repeating the viscosity measurements several times for each solute. In addition to the organic matters all solutions contain 0.1 normal potassium chloride which serves as the conducting material. In each case the conductivity of the solutions of no potassium chloride was determined in order to know the correction value for the conductivity of the electrolytes which existed in the organic matter as impurities, and such a value was subtracted from the conductivity of the solution containing potassium chloride. The results are shown in the following table.

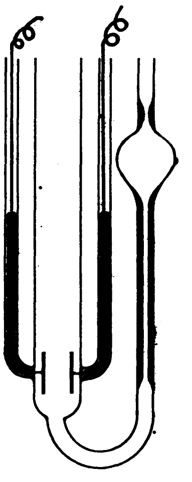

Fig. 1.

Solutes	Density d_4^{25}	Relative viscosity	Specific conductivity
KCl (0.1 N.) only	1.0019	1.005	0.01288
KCl (0.1 N.) and ethyl alcohol (ca. 50% in volume)	0.9278	2.50	0.00441
,, ,, glycerine (ca. 35% in volume)	1.0825	2.50	0.00580
,, ,, mannite (ca. 30% in wt., supersaturated)	1.1030	2.59	0.00621
,, ,, cane sugar (ca. 30% in weight)	1.1160	2.50	0.00654
,, ,, gum arabic (ca. 5.5% in weight)	1.0208	2.50	0.01160
,, ,, soluble starch (ca. 1% in weight)	1.0052	2.43	0.01235
,, ,, gelatine (ca. 3.4% in weight)	1.0113	2.47	0.01286

From the above table we see, in general, that the heavy solute molecules give less effect on conductivity than the light molecules, provided the viscosity being the same. Of course there is a great effect of solvent on dissociation degree of electrolyte, so the conductivity is influenced not only by the viscosity but also by the dissociation degree. Among the colloidal solutions gum arabic give stronger effect than gelatine, consequently the former may have lighter " molecular weight " than the latter,

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(1) Dumanski, *Z. physik. Chem.*, **60** (1907), 553.

Summary.

There are two kinds of viscosities, viz. the true viscosity and the colloidal viscosity. They can be distinguished by the conductivity measurements. The true viscosity give strong effect on the conductivity but the colloidal viscosity give slight effect on it.

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ON THE DERIVATION OF ADSORPTION ISOTHERMS. II.

By **Bun-ichi TAMAMUSHI.**

Received November 17, 1926. Published December 28, 1926.

In the previous work⁽¹⁾ the author has remarked that an exponential adsorption isotherm $C=ku^i$ could be derived from the equation of Gibbs, if we assume at the same time, the following relation,

$$(\gamma_0-\gamma)\frac{1}{u}=iRT \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

in which $(\gamma_0-\gamma)$ is the difference between the surface tension of solvent and that of solution, u the excess of solute per unit area in the surface, R the gas constant, T the absolute temperature and i a certain constant, the physical meaning of which remains to be explained.

Now the diminution in the surface tension by the adsorption film can be put equal to the pressing force P_s, across unit length of the boundary, and u the reciprocal of the adsorption surface A where the adsorption of one mol of solute takes place. So that equation (1) will be written down as follows, the correction i being dropped,

$$P_sA=RT. \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

This is known as the equation for the so-called "gaseous film," and it holds when the solution is sufficiently dilute and the average kinetic energy in each degree of freedom in the surface, $\frac{1}{2}RT$ for each molecule, acts wholly to produce the pressing force on the boundary. When the solution becomes more concentrated, due corrections are necessary. In this respect, the intermolecular forces are to be taken into account in the first place, so that we have the following relation instead of equation (2):

$$\{P_s-f(E)\}A=RT \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

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(1) Tamamushi, this journal 1 (1926), 185.

where $f(E)$ is a certain function which represents cohesion or repulsion between molecules. Certainly it is difficult to give this function a complete elucidation. At any rate, we can probable consider that molecules are electric dipoles and that there takes part potential energy of electric nature in the surface besides the thermal kinetic energy. Here let us assume that the polarization of dipole molecules in the surface is proportional to $\sqrt{A}$ i.e. to the mean distance between the molecules. Now, one end of the dipole molecules being attracted by the main body of the solution, the charge of the same sign will be arranged in the surface, the effect of which weakens the surface attraction. Let us further assume that the probability of a molecule in taking proper orientations fully to display this effect of polarization is proportional to $\sqrt{T}$, in other words, to the mean velocity of the molecule. The repulsive effect of a molecule will then be proportional to $\sqrt{A}\cdot\sqrt{T}$, and consequently the repulsive force between adjacent molecules can be represented by $q\frac{(\sqrt{A}\cdot\sqrt{T})^2}{A^2}$ or by $q\frac{T}{A}$, where q is a proportional constant.

If this expression is put into equation (3) in place of $f(E)$, the following relation will be obtained,

$$\left(P_s-\frac{qT}{A}\right)\cdot A=RT$$

or

$$P_s\cdot A=RT+qT$$

And if we put here

$$1+\frac{q}{R}=i \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (4)$$

we have

$$P_s\cdot A=iRT.$$

This is no other than equation (1).

Taking now Volmer's surface correction β into account and using the notations already mentioned, we obtain.

$$(\gamma_0-\gamma)\left(\frac{1}{u}-\beta\right)=iRT \quad\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

as a general form of the characteristic equation of the surface.

Eliminating γ from this equation and the equation of Gibbs introduced with the surface correction β i.e.

$$\frac{u}{1-u\beta}=-\frac{C}{RT}\frac{d\gamma}{dC}$$

we obtain a new adsorption isotherm as follows:

$$\frac{u}{1-u\beta}=KC^{\frac{1}{i}} \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

in which K and i are constants.

This formula is identical with that of Freundlich when u is small and it also expresses the state of saturation.

An example of the application of this isotherm for experimental data is given in the following. The data here referred are taken from one of the series of experiments made by Schmidt⁽¹⁾ on the adsorption of acetic acid solution by animal charcoal. For the convenience sake of calculation, the formula (6) is transformed into

$$\log\left(\frac{1}{u}-\frac{1}{S}\right)=\frac{1}{i}\log\left(\frac{1}{C}\right)-\log K \cdots\cdots\cdots\cdots (7)$$

in which $\frac{1}{S}=\beta$, S representing the amount of solute in saturation. And u is assumed to be proportional to the adsorption per unit mass of solvent.

Fig. 1.

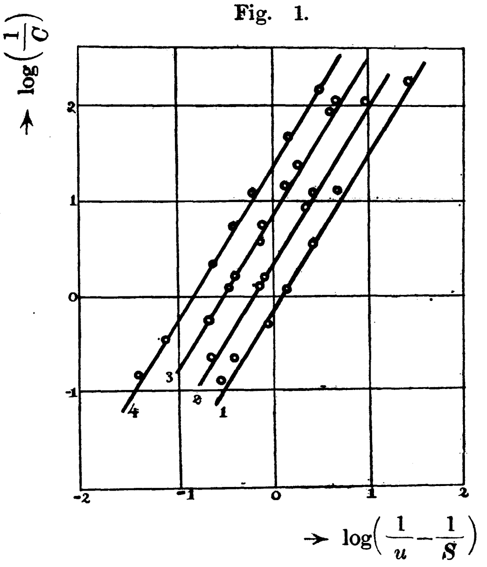

TABLE 1. 5 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{obs.}$	$C_{calc.}$
$\bar{1}$.12188	$\bar{1}$.54637	7.553	11.07
$\bar{1}$.37469	$\bar{1}$.57519	4.220	6.898
$\bar{1}$.69272	$\bar{1}$.95665	2.029	1.510
0.07058	0.14259	0.850	0.720
0.53611	0.41380	0.291	0.244
1.12148	0.69346	0.0756	0.0751
2.20761	2.42586	0.0062	0.0043
$S=0.523$	$\underline{i=1.73}$	$\underline{K=0.86}$	

TABLE 2. 10 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{obs.}$	$C_{calc.}$
$\bar{1}$.34008	$\bar{1}$.39445	4.570	4.650
0.10237	$\bar{1}$.90795	0.790	0.774
0.17393	$\bar{1}$.92788	0.670	0.555
0.95078	0.34439	0.112	0.106
1.11238	0.41731	0.0772	0.0789
2.03152	1.00689	0.0093	0.0076
$S=1.058$	$\underline{i=1.73}$	$\underline{K=1.7}$	

TABLE 3. 20 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{obs.}$	$C_{calc.}$
$\bar{1}$.76700	$\bar{1}$.38453	1.710	1.466
0.11930	$\bar{1}$.57634	0.759	0.682
0.29826	$\bar{1}$.64972	0.5032	0.5087
0.56019	$\bar{1}$.81558	0.2753	0.2627
0.73731	$\bar{1}$.90956	0.1831	0.1807
1.18442	0.10789	0.0654	0.0819
1.40561	0.26670	0.0393	0.0435
1.97551	0.59051	0.01058	0.01198
2.04096	0.65591	0.00910	0.00923
$S=2.119$	$\underline{i=1.73}$	$\underline{K=3.4}$	

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(1) Schmidt, *Z. physik. Chem.* 77 (1911), 645.

TABLE 4. 40 gr. Animal Charcoal.

$\log\frac{1}{C}$	$\log\left(\frac{1}{u}-\frac{1}{S}\right)$	$C_{obs.}$	$C_{calc.}$
$\bar{1}.21746$	$\bar{2}.61278$	6.06	8.50
$\bar{1}.56177$	$\bar{2}.89873$	2.74	2.72
$\bar{1}.69486$	$\bar{1}.02160$	2.02	1.67
0.36005	$\bar{1}.39410$	0.437	0.378
0.76447	$\bar{1}.62024$	0.172	0.158
1.12726	$\bar{1}.79078$	0.0746	0.0778
1.69680	0.17638	0.0201	0.0225
2.18046	0.51068	0.0066	0.0104

$S=4.434$ $\underline{i=1.73}$ $\underline{K=7.1}$

Fig. 1. shows that the linear relation between $\log\left(\frac{1}{u}-\frac{1}{S}\right)$ and $\log\left(\frac{1}{C}\right)$ is satisfactory. i Is found to be fairly constant for varying amounts of adsorvent and approximately equal to 1.73. The value of K found is almost proportional to the amount of charcoal taken. In the last two columns of each table the values of concentration C (gr. in 100 c.c.) are compared with that which are calculated by relation (7).

The present note, although still incomplete, is published, the author being obliged to put off further investigations for few months. In conclusion, the author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance.

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SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS.⑴
PART I.

By Taku UEMURA, Naomichi YOKOJIMA, and
Chinyü TAN.

Received November 3, 1926. Published December 28, 1926.

Introduction. The authors have studied on the relation between the colour of hydroxyazo-compounds and their chemical constitution by the spectrochemical method.

Hewitt,⑵ Baly,⑶ and Sircar⑷ already chemically investigated some hydroxyazo-compounds with regard to their chemical constitution, and

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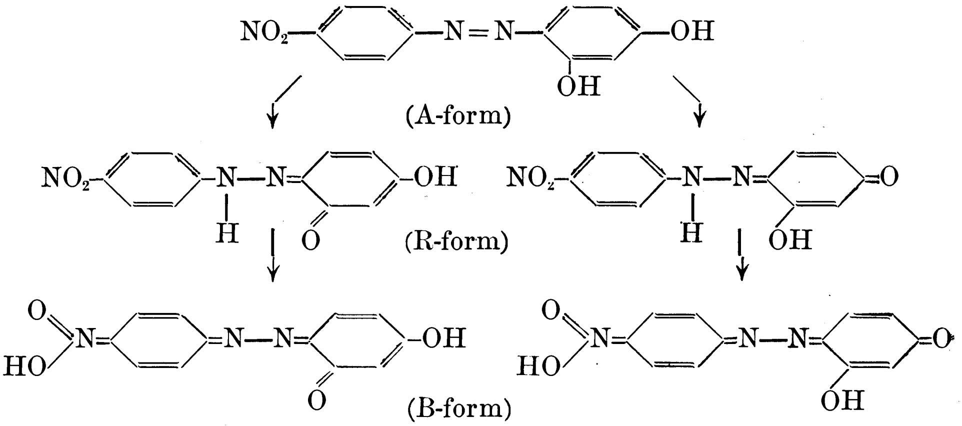
⑴ Read before the Chemical Society of Japan, October 9, 1926.

⑵ Hewitt and Mitchell, *J. Chem. Soc.*, 91 (1907), 1251.
Hewitt and Fox, *J. Chem. Soc.*, 93 (1908), 333.
Hewitt and Thomas, *J. Chem. Soc.*, 95 (1909), 1292.
Hewitt and Thole, *J. Chem. Soc.*, 95 (1909), 1393; 97 (1910), 511.

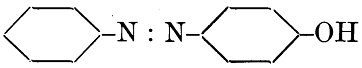
⑶ Baly, Tuck, and Marsden, *J. Chem. Soc.*, 97 (1910), 1497.

Tuck(1) did it spectrochemically. They all recognised the tautomeric changes in these compounds. K. Suitsu(2) recently observed three different colours of para-red (p-nitrobenzeneazo-β-naphthol) by changing conditions, and he respectively assigned the azo-, monoquinonoid- and diquinonoid-form to the three tautomers. We also have been able to observe the remarkable analogy in many simpler hydroxyazo-compounds and have then given the following forms respectively :



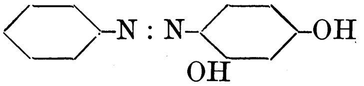
Experimental.

1. p-Hydroxyazobenzene,(3)



A dilute neutral alcoholic solution of the substance is yellow, and changes into a deeper shade by adding a KOH-solution. As the absorption curve of its N/10000 solution shows, the bathochromic and hyperchromic influences are easily observed by the addition of alkali (Fig. 1). We give A-form to the neutral solution and R-form to the alkaline.

2. Benzeneazoresorcinol,(4)



Bathochromic and hyperchromic effects due to alkali are also seen in Fig. 2, and the curve analogous to that of No. 1 compound (Fig. 1) was obtained. A- and R-forms can then be respectively assigned to neutral and alkaline solutions.

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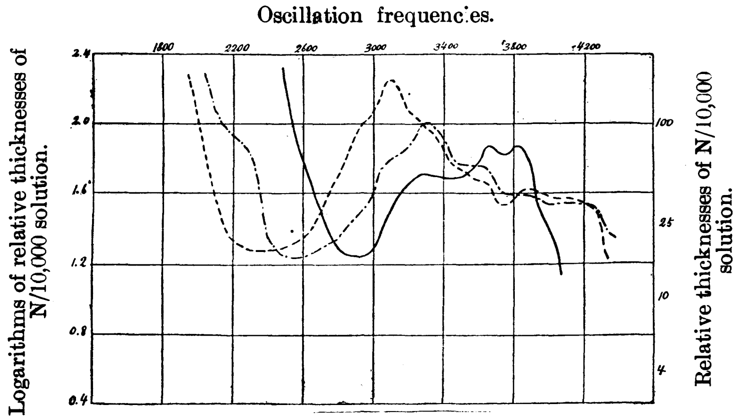
(1) Tuck, *J. Chem. Soc.*, 91 (1907), 449; 95 (1909), 1809.

(2) Suitsu and Okuma. *J. Soc. Chem. Ind. Japan*, 29 (1926), 132.

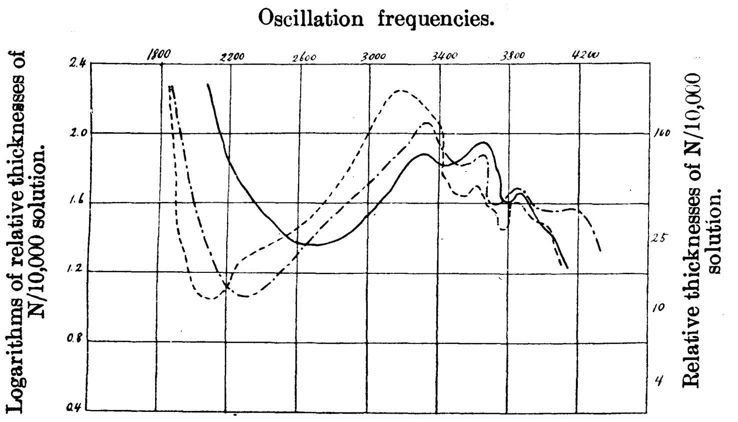
(3) Beilstein, " Handbuch der Organischen Chemie," IV (1899), 1407.

(4) Ibid., IV (1899), 1441.



1. p-Hydroxyazobenzene.	——	Neutral Solution.
	- - - - -	0.9 N. Alkaline Solution.
4. p-Nitrobenzeneazophenol.	–·–·–	Neutral Solution.

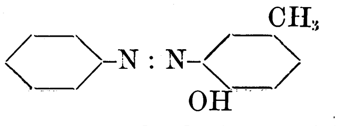
Fig. 1.



2. Benzeneazoresorcinol.	——	Neutral Solution.
	- - - - -	0.9 N. Alkaline Solution.
5. p-Nitrobenzeneazoresorcinol.	–·–·–	Neutral Solution.

Fig. 2.

3: Benzeneazo-p-cresol,⁽¹⁾



By adding KOH, the yellow neutral solution of this compound changes into red, but not blue. Two absorption bands (Fig. 3) can be observed in its neutral solution and they become clearer when we add KOH to it. We can give A-form to the yellow solution and R-form to the red one.

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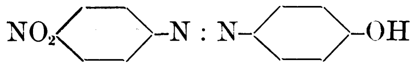
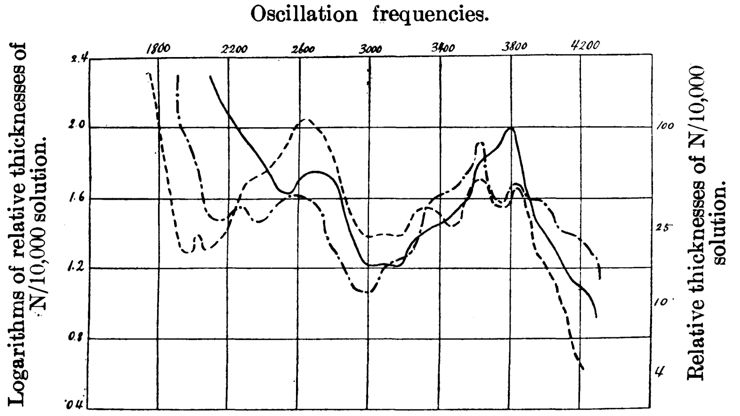
(1) Beilstein, "Handbuch der Organischen Chemie," IV (1899), 1420.

4. p-Nitrobenzeneazophenol,⑴

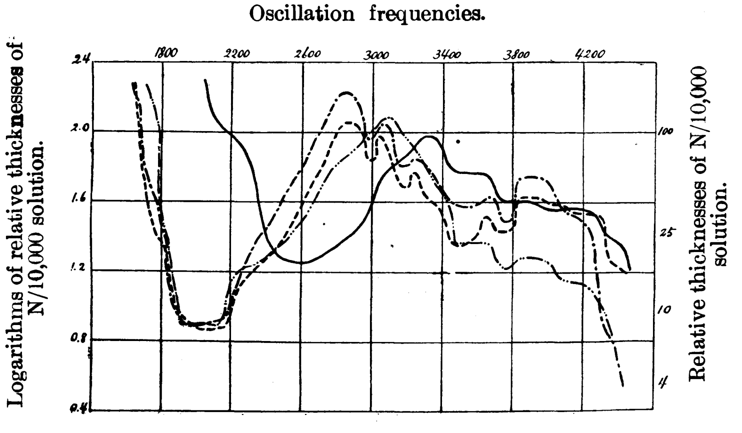


This substance undergoes quite the same change in colour as the abovementioned compounds and like them cannot obtain blue tautomer. Hewitt⑵ once gave B-form to the red solution of this compound, but according to our examination we can only give R-form to this red solution, for we can ascertain that the curve of this alkaline solution coincides to that of the red one of m-nitrobenzeneazoresorcinol (No. 6 compound) which cannot take B-form (Fig. 4).



3. Benzeneazo-p-cresol. { ——— Neutral Solution. - - - - 0.9 N. Alkaline Solution.
7. p-Nitrobenzeneazo-p-cresol. -·-·- Neutral Solution.

Fig. 3.



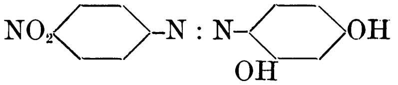
4. p-Nitrobenzeneazophenol. { ——— Neutral Solution. - - - - N/500 Alkaline Solution. -·-·- 1.44 N. Alkaline Solution.
6. m-Nitrobenzeneazoresorcinol. -··-·- 2 N. Alkaline Solution.

Fig. 4.

⑴ Ibid., IV (1899), 1410.

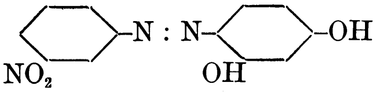
⑵ Hewitt and Mitchell, *J. Chem. Soc.*, **89** (1906), 17.

5. p-Nitrobenzeneazoresorcinol,(1)

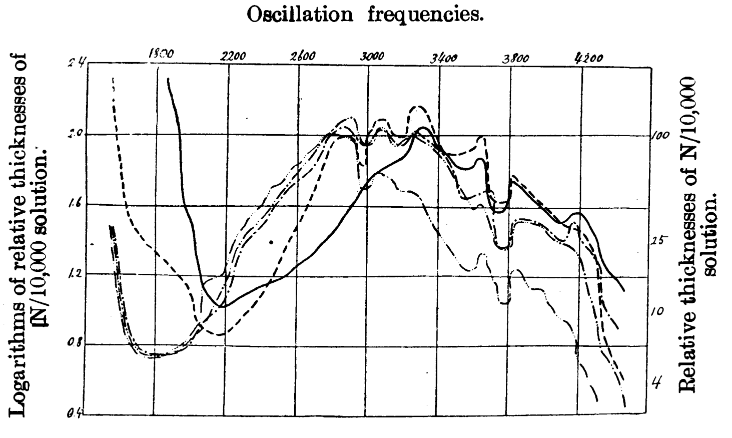


The reddish yellow neutral solution becomes red when it is N/500 alkaline solution, and bluish violet by adding a stronger alkali. Then we may respectively assign A-, R- and B-forms to these three tautomers (Fig. 5).

6. m-Nitrobenzeneazoresorcinol,(2)



The curve of N/500 alkaline solution of No. 5 compound and that of the alkaline solution of this substance nearly coincide and, therefore, this substance has A- and R-forms (Fig. 6). This compound has no B-form, for the nitro-group, in this substance takes the meta-position with respect to the azo-group, and cannot, of course, be of the isonitroform. As the three compounds (No. 2, No. 5 and No. 6), already described, have two hydroxyl-groups (ortho and para with respect to the azo-group), we may suppose two cases of tautomeric changes, but cannot yet definitely say whether it is the hydrogen atom in para hydroxyl that moves or the one in the ortho hydroxyl.



5. p-Nitrobenzeneazoresorcinol.

- ——— Neutral Solution.
- - - - - - N/500 Alkaline Solution.
- —·—·— N/20 Alkaline Solution.
- —··—··— 1 N. Alkaline Solution.
- —···—···— 5 N.Alkaline Solution.

Fig. 5.

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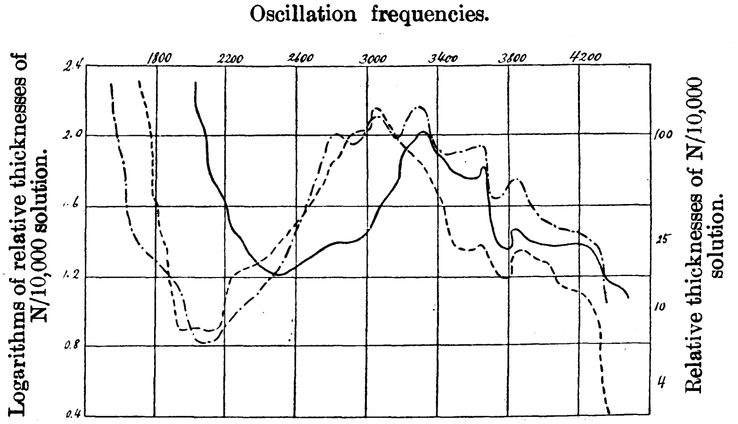
(1) Beilstein, "Handbuch der Organischen Chemie," IV (1899), 1442.

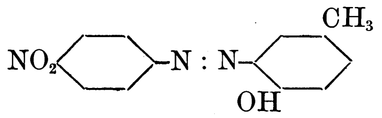
(2) Obtained from m-nitraniline and resorcinol.



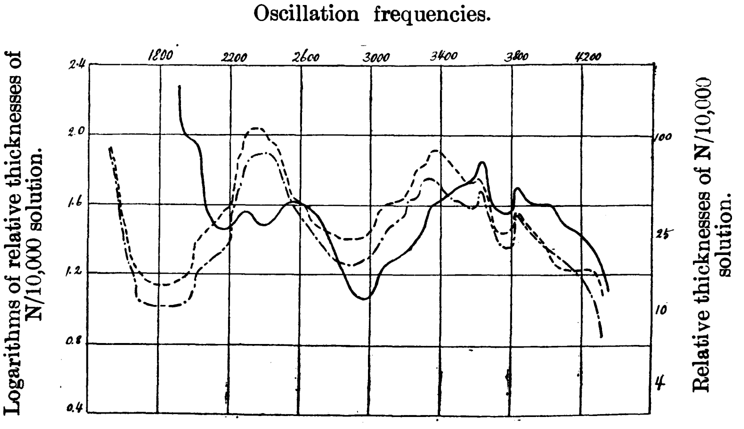
6. m-Nitrobenzeneazoresorcinol. { ——— Neutral Solution.
{ - - - - - 2 N. Alkaline Solution.
5. p-Nitrobenzeneazoresorcinol. —·—·— N/500 Alkaline Solution.

Fig. 6.

7. p-Nitrobenzeneazo-p-cresol,(1)



The yellow neutral solution changes into red and instantly into violet by adding KOH. N/1000 alkalien solution shows already a bluish violet shade. The curve of this compound (Fig. 7) has two absorption bands like that of



7. p-Nitrobenzeneazo-p-cresol. { ——— Neutral Solution.
{ - - - - - N/1000 Alkaline Solution.
{ —·—·— 0.9N. Alkaline Solution.

Fig. 7.

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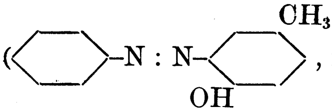
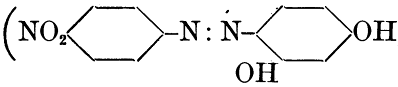
(1) Beilstein, " Handbuch der Organischen Chemie," IV (1899), 1041.

No. 3 compound (, in Fig. 3). The absorption curve of 1 N. alkaline solution of No. 5 compound (, in Fig. 5) to which was assigned B-form, nearly coincides to that of 0.9 N. alkaline solution of this compound, which is only more hypochromic than the former, and we have given A- and B-forms to this compound according to the condition. Of course, we may recognise the existence of R-form which is very unstable.

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