



Y. Ozawa

PROFESSOR YUKICHI OSAKA.

Professor Yukichi Osaka, who has recently celebrated his sixtieth birthday and retired from the Chair of Physical Chemistry at Kyoto Imperial University, was born on December 22nd in the second year of Keio (January 27th, 1867), at Daishoji in the Province of Kaga, Japan. He was the second son of Heihachi Amaya, and was adopted by his uncle, Nagashi Osaka, who belonged to one of the most honorable families in his province, as his heir. From his boyhood, Yukichi Osaka was distinguished for diligence and earnestness in his studies, manifested always by his superiority over the rest of his class. He came to Tokyo in 1885 and finished his general education there; he then took the course of chemistry from 1889 to 1892 at Tokyo Imperial University, where he was greatly influenced by his master, Professor Joji Sakurai, the present President of the Imperial Academy and a Privy Councillor. Professor Sakurai is a great personage in present-day Japan and his name must be placed in the first rank among the names of those who have actively promoted the progress of Science in Japan, particularly in the domain of Chemistry. The master's influence always remained throughout the later career of his pupils, and it was so with Professor Osaka. His paper on "Acidimetry of Hydrogen Fluoride", the result of a piece of research conducted in collaboration with Prof. T. Haga and published in the Journal of the Chemical Society of London in 1895, was his first contribution to science. In the autumn of 1892, he was appointed to the professorship of chemistry at the Fifth High School in Kumamoto, where he remained till 1896. On his return to Tokyo, he was appointed to the Chair of the same subject at the Higher Normal School in Tokyo, and in 1899 he was sent as a government student to Europe, where he studied physical chemistry under Professor W. Ostwald at Leipzig University, and under Professor Nernst at Göttingen University. This was the most brilliant epoch in the development of classical physical chemistry; its importance was daily increasing as a new branch of science and excellent works in this field were appearing day by day. Many students from all parts of the world gathered under Professors Ostwald and Nernst; Dr. Osaka worked among them, and his indefatigable industry resulted in the publication of several important papers, some of which will be referred to later on. After his return to Japan in 1902 he remained one year in the Higher Normal School in Tokyo, and received the degree of Rigakuhakushi (D. Sc.). In the autumn of 1903, he was appointed to the Chair of Applied Electro-chemistry at Kyoto Imperial University, and in the following spring,

he was transferred to the Chair of Physical Chemistry at that university, which had been rendered vacant by the death of its first occupant, Professor Kenjiro Ota. For more than twenty three years, he occupied this chair as one of the most eminent investigators and teachers in this university until his sixtieth birthday, December 22nd, 1926, when, having attained the age limit, he retired. Soon after this, he received the honour of being elected a Professor Emeritus of this university. From 1916 to 1918 he was the Dean of the Science Department of this university, and under his administration, the department underwent a great development by the addition of the institutes of Zoology and Botany.

Recalling the researches which he has contributed for the benefit of science, we must first point out two particularly excellent papers: The first is "Ueber die Birotation der d-Glukose", which has now become a well-known classical work upon the catalysis of the hydroxyl ion. He showed that the decrease of the rotation of several kinds of sugars proceeds with time by the formula of unimolecular reaction, and that the velocity of the decrease of the rotation of d-glucose is accelerated by the presence of each of the hydrogen and hydroxylions, the effect of the latter being strikingly great. He pointed out that the measurement of this decrease of rotation is therefore one of the most accurate methods of determining the hydroxylion. The other paper is "Ueber anodische Oxydation von Metallen und elektrolytische Sauerstoffentwicklung," published jointly with Professor A. Coehn. They investigated the phenomenon of overvoltage in the discharge of an anion such as the hydroxyl ion on metal surfaces, and described the remarkable behaviour of nickel with which the solution of potassium hydroxyde decomposes at about 1.3 volts while with platinum it requires about 1.7 volts. This is also a classical paper on anodic over-voltage.

During his active service at Kyoto Imperial University, very many papers were published under his own name or under those of his pupils. Special attention is called to his works relating to some heterogeneous equilibria, especially on the systems: salts and water, to which he devoted much time, thought and labour. The scientific importance of such works is so clear that there is no need here to dilate on it, but when we recollect that such investigations had great practical value also, especially in the time of the Great War, we can see how paramount are the investigations in this field, and can appreciate the great merit of his original contributions. So far as Dr. Osaka himself was concerned, however, the technical application of his researches was entirely outside his purpose. The serenity of his character and the keenness of his love of science are clearly manifest in his selection of subjects for research, and in his mode of investigation throughout his scientific career. Only by dint of his keen love of science, was he

able to accomplish the solution of some of the very complicated systems of equilibrium treated.

He was not only an able investigator, but at the same time, he was an excellent teacher and research director, always in the laboratory, going from one student to another, arousing and maintaining their interest in the work, and ready to discuss with them any point of difficulty arising out of their studies. His attitude toward any student of his was really that of a father to his son, and no one who had once worked in his laboratory ever could put out of his mind the happy memory of his master, nor fail to maintain his devotion toward that master forever throughout life. His helpfulness on all occasions was not limited to the inside of the laboratory only; all friends and students entertain a vivid impression of his cheerfulness and good humour, of his private charity and benevolence, and of his simplicity of manner and purity of life.

He was also deeply interested in the teaching of chemistry in general, and wrote an excellent text book of chemistry for middle schools, the first edition being published as early as 1897, including many ideas of physical chemistry, which were at that time not popular in that grade of chemistry teaching. It was his opinion (also that of his master, Professor Sakurai) that the principal ideas of physical chemistry ought to be included in the chemistry taught in secondary schools; and owing to their efforts the importance of physical chemistry is more widely recognized here in Japan than, perhaps, in any other country. From that time till now, his text-book has been so popular, that most young Japanese of to-day have learned chemistry for the first time in their lives out of this text-book, always receiving great influence from it. This service rendered by him for the development of chemistry in Japan is no less meritorious than that of his scientific work.

Since retirement, he has been enjoying his leisure in perfect health, surrounded by his happy family in a peaceful environment; he is still devoting the better part of his time to aiding in the general development of chemistry in Japan.

Shinkichi HORIBA.

EQUILIBRIA IN THE SYSTEMS CONTAINING WATER AND CHLORIDES OF IRON, COBALT AND NICKEL AT 25.0°. ⁽¹⁾

By Yukichi OSAKA and Tokuzo YAGINUMA.

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Iron, cobalt and nickel form one of the three triads in the eighth group of the periodic system of the chemical elements and they have many similarities in their chemical behaviours. We have undertaken to study the equilibria in the systems of their chlorides and water, as, so far as we know, there has been no systematic study about them.

As to the equilibrium of the system of ferrous chloride, nickel chloride and water at 25°, we have found that they form two series of solid solutions, one on the side of ferrous chloride with four molecules of water of crystallisation and the other on the side of nickel chloride with six molecules of it, and have reported the result lately in the "Cohen-Festband" of the *Zeitschrift für physikalische Chemie*. ⁽²⁾

In this article we will report on the equilibria in the following systems at 25.0°:

1. FeCl_3 , CoCl_2 , and H_2O ,
2. FeCl_3 , NiCl_2 , and H_2O ,
3. CoCl_2 , NiCl_2 , and H_2O ,
4. FeCl_3 , CoCl_2 , NiCl_2 , and H_2O .

Materials. Ferric chloride from C. Merck was twice recrystallised after Roozeboom. ⁽³⁾ Of cobalt chloride and nickel chloride, the purest preparations (each free from the other) of Kahlbaum was directly used. The ordinary distilled water was used.

Procedure. The usual procedure as ordinarily carried out in our laboratory and reported in several previous papers was employed.

Analysis. The *total chlorine* was determined by Volhard's method modified by V. Rothmund and A. Burgstaller. ⁽⁴⁾ When the solution was faintly pink coloured by an excess of the cobalt salt, it was removed by an addition of a proper quantity of nickel nitrate, and vice versa, and the titration could be carried out in the presence of cobalt and nickel.

(1) The experimental work of this article was performed in the Physico-chemical Department of the Chemical Institute, Kyoto Imperial University, in 1926.

(2) *Z. physik. Chem.*, **130** (1927), 480.

(3) *Z. physik. Chem.*, **10** (1892) 477.

(4) Treadwell-Hall, "Analytical Chemistry." Vol. 2. 4th ed., p. 703.

The *nickel* was determined by the Tschugaeff's reaction between nickel salt and dimethyl glyoxime.⁽¹⁾

The *iron*. The ferric salt was first reduced to the ferrous salt with stannous chloride and after proper treatments was finally titrated with potassium permanganate.⁽²⁾

The *cobalt* was estimated from the total chlorine and the quantities of iron and nickel.

Results.

1. The System : $\text{FeCl}_3\text{—CoCl}_2\text{—H}_2\text{O}$.

The result is given in Table 1.

TABLE 1.

No.	Solution.			Wet residue.			Dry residue.
	FeCl_3	CoCl_2	H_2O	FeCl_3	CoCl_2	H_2O	
1	0.00	36.08	63.92	—	—	—	$\text{CoCl}_2.6\text{H}_2\text{O}$
2	7.77	29.36	62.87	3.65	44.86	51.49	⤵
3	19.08	20.95	59.97	4.95	46.09	48.96	⤵
4	35.52	10.13	54.35	8.79	44.32	46.89	⤵
5	41.07	7.99	50.94	12.20	41.04	46.76	⤵
6	43.28	7.40	49.32	50.07	6.61	43.32	} $\text{CoCl}_2.6\text{H}_2\text{O}$ and $\text{FeCl}_3.6\text{H}_2\text{O}$
7	43.34	7.45	49.21	45.22	11.89	42.89	
8	43.95	6.58	49.47	55.46	2.03	42.51	$\text{FeCl}_3.6\text{H}_2\text{O}$
9	44.50	5.99	49.51	54.37	2.03	43.59	⤵
10	47.17	2.47	50.36	56.04	0.48	43.48	⤵
11	51.57	4.74	43.69	16.36	54.48	29.16	} $\text{CoCl}_2.2\text{H}_2\text{O}$] $\text{FeCl}_3.6\text{H}_2\text{O}$
12	49.42	0.00	50.58	—	—	—	

In this and the following tables the compositions are give in gram percentages. A labile residue is enclosed in brackets. The result is graphically represented in Fig. 1.

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- (1) E. Grossmann, "Die Bestimmungsmethoden des Nickels and Cobalts und ihre Trennung von der anderen Elementen." Pp. 91, 120; O. Brunk, *Z. angew. Chem.*, **20** (1907) 834.
 (2) Treadwell-Hall, *loc. cit.*, p. 610.

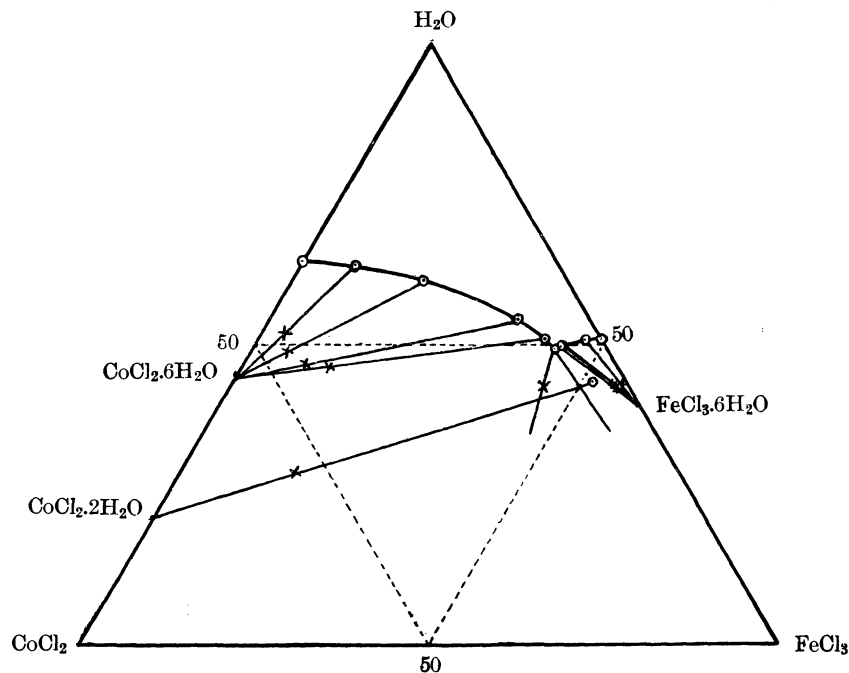


Fig. 1.

These chlorides do not form any double salt nor any solid solution as may be expected. Each forms only the hexahydrates even in the saturated solution of the other. The existence of a labile dihydrate was observed.

2. The System : $\text{FeCl}_3\text{—NiCl}_2\text{—H}_2\text{O}$.

The result is given in Table 2 and graphically in Fig. 2.

TABLE 2.

No.	Solution.			Wet residue.			Dry residue.
	FeCl_3	NiCl_2	H_2O	FeCl_3	NiCl_2	H_2O	
1	0.00	38.88	61.12	—	—	—	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
2	10.24	30.89	58.87	2.36	49.07	48.57	„
3	22.68	22.21	55.11	5.47	46.98	47.55	„
4	26.33	19.86	53.81	7.81	47.18	45.01	} $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$
5	26.49	19.75	53.76	9.14	47.62	43.19	
6	29.77	18.11	52.12	9.19	43.90	46.91	
7	31.35	16.43	52.22	9.94	49.68	40.38	$[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$
8	37.47	11.88	50.65	13.40	45.55	41.05	$\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$
9	40.65	10.73	48.62	22.32	27.36	40.31	} $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
10	40.61	10.69	48.72	44.22	15.59	40.19	
11	42.22	9.89	47.89	15.29	44.34	40.37	
12	46.24	7.33	46.43	16.04	44.52	39.44	$[\text{NiCl}_2 \cdot 4\text{H}_2\text{O}]$
13	41.01	10.01	48.98	54.33	2.80	42.87	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
14	43.39	6.80	49.81	—	—	—	„
15	46.08	4.37	49.55	54.86	1.11	44.03	„
16	49.42	0.00	50.58	—	—	—	„

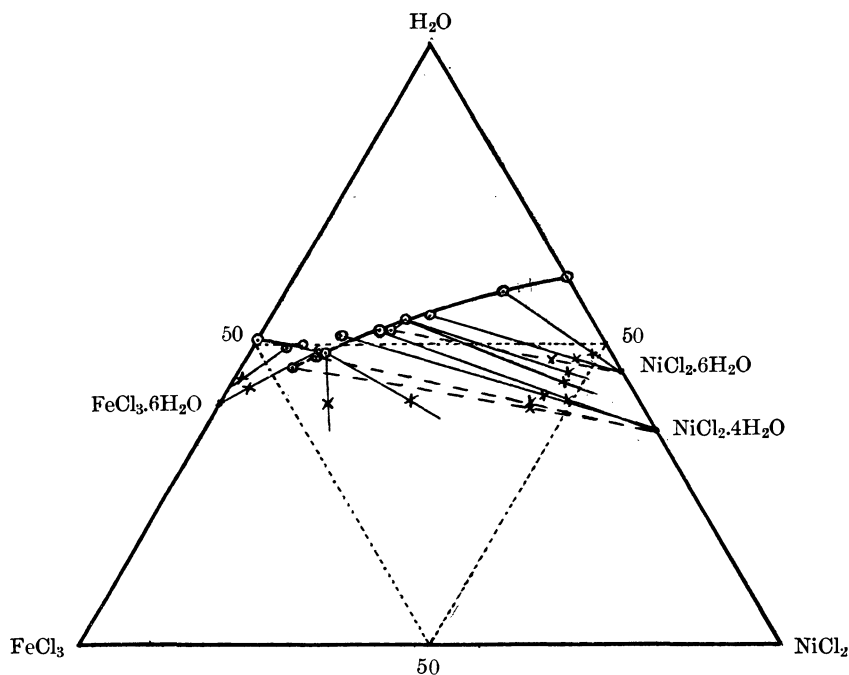


Fig. 2.

In this table the labile residues are enclosed in brackets. In this case also no double salt nor solid solution was observed as may be expected. The both chlorides are hexahydrated, but when the concentration of ferric salt is increased, nickel chloride becomes tetrahydrated.

3. The System: $\text{CoCl}_2\text{—NiCl}_2\text{—H}_2\text{O}$.

The result is given in Table 3 and graphically in Fig. 3.

TABLE 3.

No.	Solution.			Wet residue.			Dry residue.
	NiCl_2	CoCl_2	H_2O	NiCl_2	CoCl_2	H_2O	
1	38.88	0.00	61.12	54.75	0.00	45.25	$\text{NiCl}_2.6\text{H}_2\text{O}$
2	34.36	4.38	61.26	41.54	12.20	46.26	$(\text{Ni, Co}) \text{Cl}_2.6\text{H}_2\text{O}$
3	31.91	6.28	61.81	34.37	19.67	45.96	„
4	30.63	7.66	61.71	32.74	21.14	46.12	„
5	26.13	11.83	62.04	25.32	28.71	45.97	„
6	22.51	14.87	62.52	18.99	34.80	46.31	„
7	13.39	23.42	63.19	9.87	44.21	45.92	„
8	10.45	26.17	63.38	7.63	46.13	46.22	„
9	4.31	32.06	63.93	1.83	51.88	46.29	„
10	0.00	36.08	63.92	0.00	54.59	45.41	$\text{CoCl}_2.6\text{H}_2\text{O}$

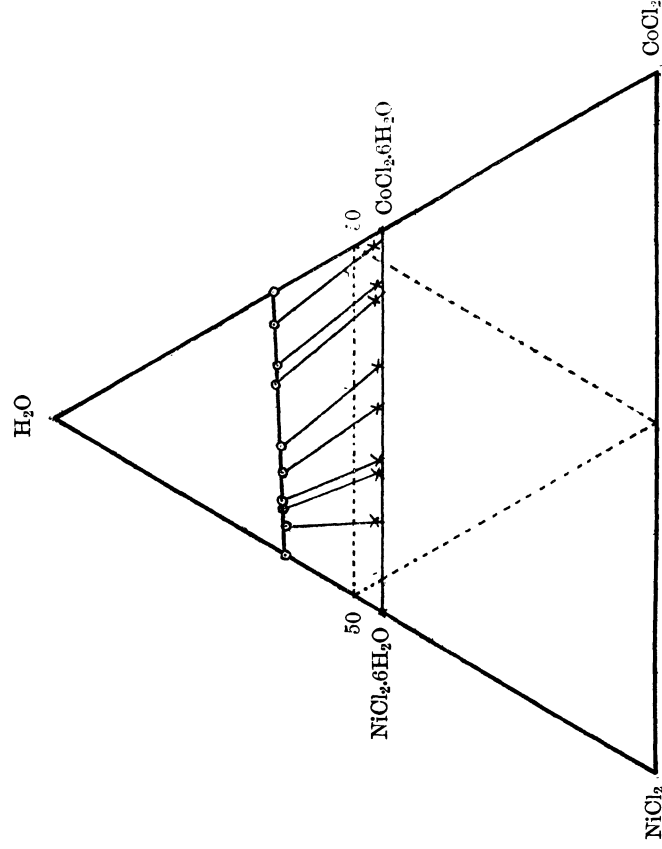


Fig. 3.

These chlorides form a complete series of solid solutions with six molecules of water of crystallisation.

4. The System : $\text{FeCl}_3\text{—CoCl}_2\text{—NiCl}_2\text{—H}_2\text{O}$.

The result is given in Table 4.

TABLE 4.

No.	Solution.				Wet residue.			
	FeCl_3	NiCl_2	CoCl_2	H_2O	FeCl_3	NiCl_2	CoCl_2	H_2O
1	40.63	10.75	0.00	48.62	—	—	—	—
2	40.61	9.79	0.50	49.10	35.22	20.85	3.61	40.32
3	40.02	8.76	1.53	49.69	32.18	17.13	8.94	41.15
4	40.71	7.50	2.90	48.89	12.62	27.52	20.58	39.28
5	40.78	5.84	4.03	49.35	29.36	9.95	16.49	44.20
6	40.44	5.92	4.89	48.75	34.61	8.85	15.38	41.16
7	41.23	4.54	5.25	48.98	21.07	9.18	28.81	40.94
8	41.31	3.98	6.00	48.71	27.38	6.58	24.55	41.49
9	40.87	3.53	6.63	48.97	11.19	8.06	34.72	46.03
10	40.71	2.98	7.58	48.73	20.97	4.81	28.53	45.70
11	41.80	1.86	7.62	48.72	33.93	1.66	20.90	43.51
12	42.35	1.29	7.31	49.05	26.82	1.16	25.33	46.69
13	40.30	0.00	7.40	52.30	—	—	—	—

The residues as analysed contained some mother liquor adhering and it was impossible to find the composition of dry residues from the data we had, but they may serve at least to ascertain that the residues contained all the three chlorides. From the Phase Theory it may be easily seen that the residues consist of two solid phases, and from what we have seen in the cases of the three component systems it is certain that one of the solid phases is ferric chloride hexahydrate and the other a solid solution of cobalt and nickel chlorides. As to the water of crystallisation in the solid solutions, we may presume that on the side of nickel chloride they contain four molecules of water of crystallisation and on the side of cobalt chloride six molecules of it, for these chlorides crystallise from the solutions saturated with ferric chloride with four and six molecules of water of crystallisation respectively.

To represent the result in a triangular diagram in the terms of the three chlorides with no regard to water, we have calculated the following table:

TABLE 5.

No.	Solution.			Solid solution.	
	FeCl ₃	NiCl ₂	CoCl ₂	NiCl ₂	CoCl ₂
1	79.07	20.93	0.00	100.00	0.00
2	79.79	19.24	0.97	85.25	14.75
3	79.95	17.08	2.97	65.88	34.12
4	79.69	14.67	5.64	57.22	42.78
5	80.50	11.53	7.97	37.63	62.37
6	78.98	11.55	9.47	36.55	63.46
7	80.79	8.89	10.32	24.16	75.84
8	80.56	7.75	11.69	21.13	78.87
9	80.08	6.91	13.02	18.84	81.16
10	79.41	5.80	14.79	14.43	85.57
11	81.50	3.63	14.87	7.34	92.66
12	83.12	2.53	14.35	4.38	95.62
13	84.48	0.00	15.52	0.00	100.00

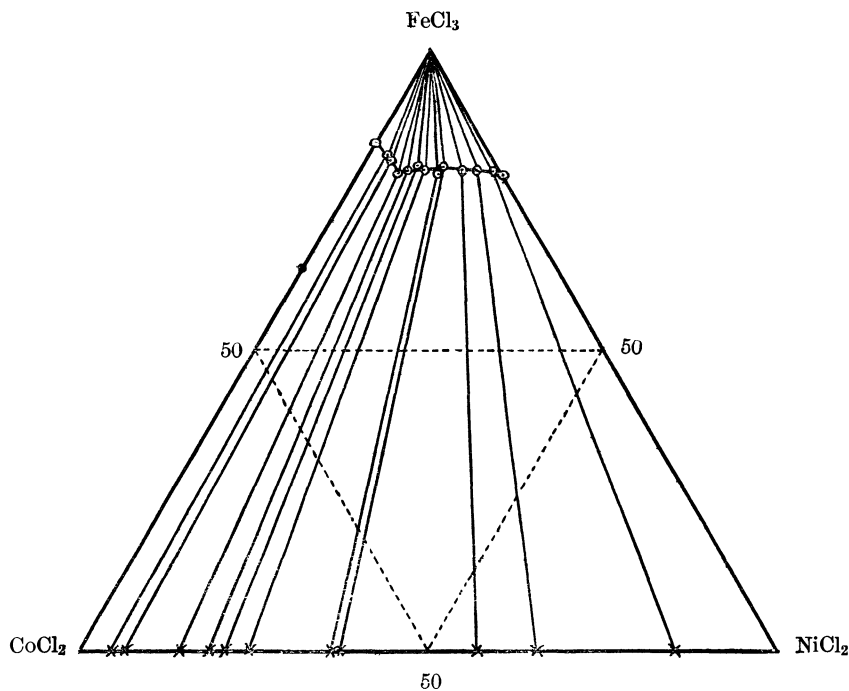


Fig. 4.

The result is graphically represented in Fig. 4. As above stated the residues are not pure, but to see an approximate relation between the solutions and the residues they were assumed to be pure in the plotting.

Summary.

The equilibria in the following systems at 25.0° have been studied :

1. $\text{FeCl}_3\text{—CoCl}_2\text{—H}_2\text{O}$,
2. $\text{FeCl}_3\text{—NiCl}_2\text{—H}_2\text{O}$,
3. $\text{CoCl}_2\text{—NiCl}_2\text{—H}_2\text{O}$,
4. $\text{FeCl}_3\text{—CoCl}_2\text{—NiCl}_2\text{—H}_2\text{O}$,

and the results have been given in tables and diagrams.

Kyoto.

THE DETERMINATION OF THE VAPOUR PRESSURES OF
SODIUM AND POTASSIUM CHLORIDES.

By Shinkichi HORIBA and Hideo BABA.

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It was hitherto considered a passably difficult bit of technique to determine directly or statically the vapour pressure of a substance when it exerts quite a small vapour pressure at a high temperature, so that, even with alkali halides, the data of those vapour pressures given in the literature,⁽¹⁾ which are not exceedingly small at above 1000°C., were still determined only by dynamical methods. One of the present writers (S.H.) used a quartz pressure indicator for the determination of the vapour pressure of metallic arsenic⁽²⁾ in the Chemical Laboratory in Amsterdam by Prof. Smits and he has now succeeded in constructing a quartz pressure indicator of the same form, whose sensitivity is acute enough to determine some fractions of mm. of mercury. In the present experiments, the writers have applied this pressure indicator to the direct or statical determination of the vapour pressures of sodium and potassium chlorides.

Samples. Sodium chloride was precipitated from the saturated solution of the "natrium chloratum" of the Japanese Pharmacopoeia by gaseous hydrogen chloride, and this precipitate was dried in an air bath and subjected to a red heat for several hours and then kept in a desiccator made up of P_2O_5 . In the case of potassium chloride, the purest sample of Kahlbaum's was recrystallised and dried in the same manner as with the sodium chloride.

The Pressure Indicator. The quartz pressure indicator used is represented by A in Fig. 1. Two glass windows were cemented exactly in the place of the pointer of the indicator, for the purpose of detecting even a minute deviation of the pointer from its zero point. Below these windows, a water condenser, shown in the figure, served for the protection from heating of the cement used to attach the glass windows.

(1) Ruff and Magdan, *Z. anorg. allgem. Chem.*, **117** (1921), 161; v. Wartenberg and Albrecht, *Z. Elektrochem.*, **27** (1921), 568.

(2) *Z. physik. Chem.*, **106** (1923), 295.

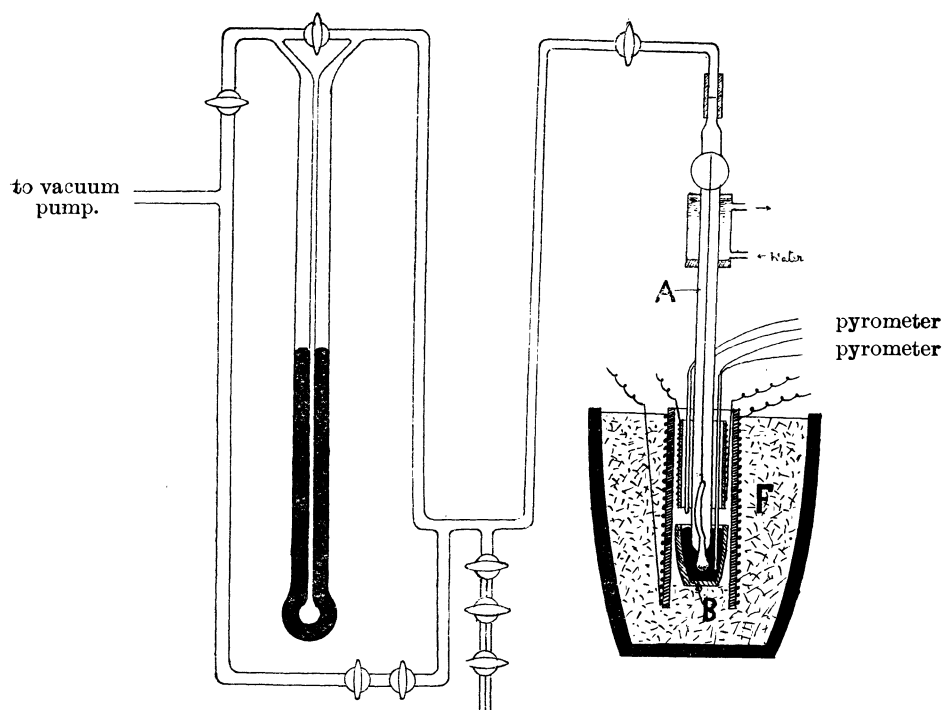


Fig. 1.

Bath and Furnace. The thermostat used was a melted silver bath, 8 cm. in depth, represented by B in Fig. 1 and it was placed in the middle of a large quartz cylinder, 7 cm. in diameter, which had nichrome wire coiled in two layers on its outside. As seen in the figure, this quartz cylinder stood in the middle of a large crucible, 30 cm. in diameter, which was completely filled with asbestos fibre F. For the protection from cooling of the upper part of the silver bath as well as for the purpose of the fine adjustment of the temperature of the furnace, an earthen-ware tube, surrounded also with a coil of nichrome wire, was hung over the silver bath.

Filling of the Sample in the Indicator. To fill up the sample in the indicator, this was at first drawn out from the furnace and the sample was put into its bulb; then the indicator was evacuated by a Langmuir pump during 7 days—9 hours per day, or a total of 63 hours; during this pumping the bulb and spring were constantly heated from outside at a temperature of about 600°C. Then keeping the indicator at a very high vacuum by means of cooling the glass tube, connected between the vacuum pump and the indicator, with liquid air, the indicator was sealed off. This procedure of the pumping is of great importance, for, in case of incomplete pumping,

the experimental results of the pressure at a high temperature were always too high, owing to minute adsorbed gases in the sample as well as in the wall of the indicator, which were exceedingly difficult to remove completely.

The Method of the Measurement. After complete melting of the silver bath by electric heating of the furnace, the bulb of the indicator was put just in the middle of the silver bath and the vapour pressure of the salt was measured in the range of temperature between 1000° and 1250°C. by the usual method as indicated in the figure. For the determination of the temperature, two platinum-platinum-rhodium thermocouples, calibrated with Sb, NaCl, Ag and Cu, were used; one of which was just put in contact with the bulb of the indicator and the other near the spring. The temperature of the spring was kept always about 5 degrees higher than that of the sample to avoid the condensation of the salt vapour on the inside wall of the spring. For the determination of the vapour pressure below 1000°C., the experiment was carried out on the out-side of the silver bath, it was, therefore, somewhat in an inferior condition in regard to the homogeneity of the temperature in comparison with the work at higher temperatures. In the experiments concerning NaCl, the measurements of the pressure could be carried out down to 800°C.; but as for KCl, not much weight could be put upon results obtained below 900°C.

The Results of the Experiments.

TABLE 1.

Vapour Pressure of NaCl.

$$\frac{Q}{4.571} = 8669, \quad C = 5.04.$$

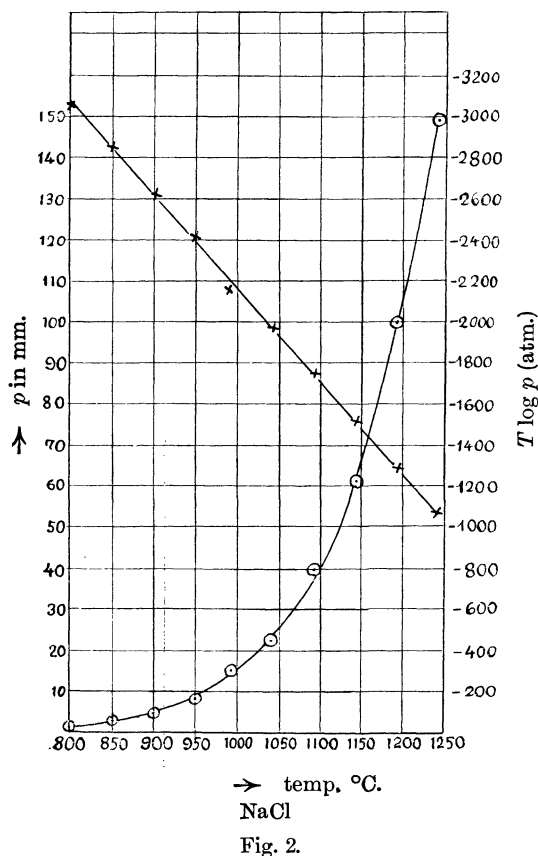
$t^{\circ}\text{C.}$	$p \text{ (mm.)}$ Hg at $t^{\circ}\text{C.}$	$T \log p \text{ (atm.)}$	$\frac{Q}{4.571}$	$\Delta \frac{Q}{4.571}$	$p \text{ (mm.) Calc.}$
800	1.	-3045	8581	- 88	1.2
850	2.5	-2851	8643	- 26	2.7
900	4.5	-2635	8787	+ 18	5.7
950	8.	-2433	8743	+ 74	6.8
991	15.	-2154	8524	- 147	11.5
1041	22.5	-2008	8629	- 48	21.5
1091	39.5	-1752	8626	- 43	31.0
1141	61.5	-1543	8669	0	61.5
1191	100	-1291	8669	0	100.0
1241	149.0	-1071	8701	+ 32	157.0

TABLE 2.

Vapour Pressure of KCl.

$$\frac{Q}{4.571} = 8007, \quad C = 4.697.$$

$t^{\circ}\text{C.}$	p (mm.) Hg at 0°C.	$T \log p$ (atm.)	$\frac{Q}{4.571}$	$\Delta \frac{Q}{4.571}$	p (mm.) Calc.
700	1.5				
750	3.				
800	4.5				
900	7.	-2394	7904	-93	5.6
950	13.	-2164	7905	-92	11.
980	16.	-2101	7986	-21	15.8
1000	21.	-1984	7964	-43	19.4
1041	32.	-1808	7981	-26	30.5
1071	41.5	-1697	8012	+ 5	42.6
1111	62.5	-1502	8007	0	62.5
1150	89.	-1325	8010	+ 3	89.9
1210	152.	-1037	8007	0	152.
1251	214.5	- 837	7996	-11	211.



Applying the Clausius-Clapeyron equation, $T \log p$

$$= -\frac{Q}{4.571} + CT, \quad \text{on the}$$

above experimental results, the constants Q and C could be determined; from this equation the vapour pressure could be then calculated, which was shown in the last column in the above tables.

Heats of Vapourisation and Dissociation. From Table 1, in the case of NaCl,

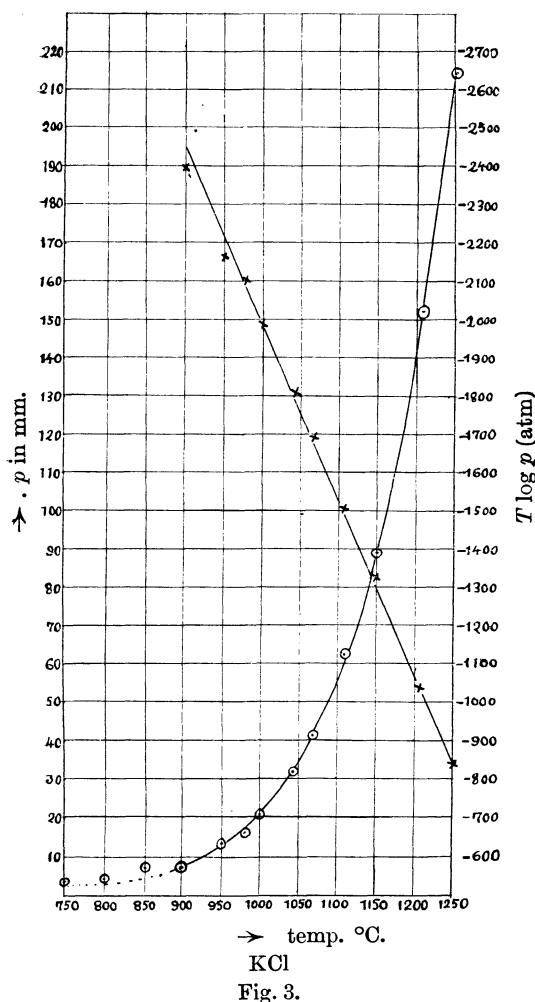
$$\frac{Q}{4.571} = 8669$$

then the heat of vapourisation of NaCl, $Q = 39.6$ Cal.

From Table 2, in the case of KCl,

$$\frac{Q}{4.571} = 8007$$

then the heat of vapourisation of KCl, $Q = 36.6$ Cal.



	U	M	Q
NaCl:	181 (Grimm u. Herzfeld) ⁽¹⁾	123.5 (Plato, Sackur, Lamplough) ⁽²⁾	39.6 (The writers)
KCl:	165 (Grimm u. Herzfeld)	86.0 (Plato, Sackur) ⁽²⁾	36.6 (The writers)

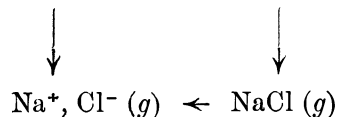
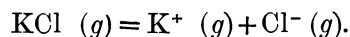
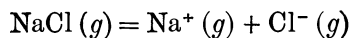
Then the heat of dissociation of gaseous NaCl:

$$D = 18 \text{ Cal.}$$

and that of KCl:

$$D = 42 \text{ Cal.}$$

Now we shall try to find the heats of dissociation of the following reactions:



Consider a cycle represented above. Then it is easily seen that the lattice energy or heat of dissociation of solid NaCl into ionic gases is equal to the sum of the heat of melting, the heat of vapourisation, and the heat of dissociation of gaseous NaCl into gaseous ions, or

$$U^* = M + Q + D$$

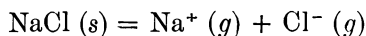
and we have,

* Here in this calculation, we have neglected the temperature dependency of U , or the difference between the specific heats of solid and gas. Speaking more precisely, see the value ΔH on the next page.

(1) *Z. Physik*, 19 (1923), 149.

(2) Landolt, "Tabellen", (1923), p. 1425.

The Dissociation Constant of NaCl. Here a rough calculation of the dissociation constant of NaCl will be given only to show the order of its value. In the reaction,



the maximum work or the decrease of the free energy is

$$\Delta A = -\Delta F = RT \ln p_{\text{Na}^+} p_{\text{Cl}^-} = RT \ln K.$$

On the other hand,

$$\Delta F = -\Delta H_p - T\Delta S,$$

where ΔH_p is the heat of this reaction and it will be expressed as follows :

$$\begin{aligned} \Delta H_p &= U_{\text{NaCl}} + 2 \times \frac{5}{2} RT - \int_0^T C_{p, \text{NaCl}} dT^* \\ &= U_{\text{NaCl}} + 2 \times \frac{5}{2} RT - 2 \int_0^{298} C_v dT - 12 \times (T - 298) \\ &= U_{\text{NaCl}} + 2 \times \frac{5}{2} RT - 2110 - 12 \times (T - 298), \end{aligned}$$

where U_{NaCl} is the lattice energy of NaCl at absolute zero degree.

Assuming that an ionic gas, such as Na^+ , Cl^- , behaves as a mono-atomic gas, we can easily calculate its entropy :

$$S = C_p \ln T - R \ln p + S_0,$$

$$\text{where } S_0 = R \left[\ln \left\{ \frac{(2\pi)^{\frac{3}{2}} k^{\frac{3}{2}}}{N^{\frac{3}{2}} h^3} \right\} + \frac{5}{2} \right]^{**} + \frac{3}{2} R \ln M,$$

$$\text{or } S = \frac{5}{2} R \ln T + \frac{5}{2} R - R \ln p + \frac{3}{2} R \ln M - R \times 3.66.$$

Then the sum of the entropies of one mol of Na and Cl each is

$$\begin{aligned} S_{\text{II}} &= 5R \ln T + 5R - 2R \ln p + \frac{3}{2} R \ln 23 + \frac{3}{2} R \ln 35.46 \\ &\quad - R \times 2 \times 3.66 \end{aligned}$$

where we put $M_{\text{Na}^+} = 23.00$; $M_{\text{Cl}^-} = 35.46$, and the term $2 \ln p$ will be left aside when the pressure of each ion is one atmosphere.

* For our present purpose, a rough calculation for the expression $\int_0^T C_{p, \text{NaCl}} dT$ is sufficient. We shall at first divide this integral into two parts, that is below and above the temperature 298°; in the part below this temperature we have $2 \int_0^{298} C_v dT = 2110$ cal. from Einstein's expression, putting $\nu = 5.81 \times 10^{12}$, while in the part above, we could put $\int_{29}^T C_{p, \text{NaCl}} dT = 12 \times (T - 298)$ approximately.

** Tolman used, in his calculation (*J. Am. Chem. Soc.*, 43 (1921), 1630) an experimental value -3.2 cal. deg⁻¹ instead of this expression, but the writers here applied the theoretical value.

Next, the entropy of solid NaCl will be calculated :

$$S_{\text{NaCl (s)}} = \int_0^T C_p d \ln T = 2.3 \int_0^T C_v \log T + 2.3 \int_0^T (C_p - C_v) \log T.$$

The value of it at 25°C.⁽¹⁾ can be calculated by Debye's formula, and we have

$$\frac{1}{2} S_{\text{NaCl (s)}} = 8.72 \text{ cal. deg}^{-1}$$

Neglecting the term $(C_p - C_v)$ and assuming that the specific heat of NaCl above 25°C.⁽²⁾ will obey Dulong-Petit's law, we have

$$S_I = 2 \times 8.72 + 2 \int_{298}^T \frac{5}{2} R d \ln T = 2 \times 8.72 + 6R \ln (T - 298)$$

Then

$$\begin{aligned} \Delta S &= S_{II} - S_I \\ &= 5R \ln T + 5R + \frac{3}{2} R \ln 23 + \frac{3}{2} R \ln 35.46 \\ &\quad - R \times 2 \times 3.66 - 2 \times 8.72 - 6R \ln (T - 298). \end{aligned}$$

Then

$$\begin{aligned} \Delta F &= U_{\text{NaCl}} + 1466 - 12 \times T + 5RT - 5RT \ln T - 5RT \\ &\quad - \frac{3}{2} RT \ln 23 - \frac{3}{2} RT \ln 35.46 + R \times 2 \times 3.66 T \\ &\quad + 2 \times 8.72 T + 6RT \ln (T - 298). \end{aligned}$$

Finally we have

$$\log K = \log [\text{Na}^+] [\text{Cl}^-] = - \frac{U_{\text{NaCl}} + 1466}{2.3 RT} + 5 \log T - 6 \log (T - 298).$$

This equation will be applied in the temperature between 25° and 800°C., and at the melting point of NaCl or 800°C. we have

$$K_{1073} = 10^{-39}$$

Summary.

The vapour pressures of NaCl and KCl up to the temperature of 1250°C. were statically determined.

The heats of vapourisation and of dissociation of these salts were calculated from the values of their vapour pressures and the order of the value of the dissociation constant of NaCl in gaseous state was given.

December 1927.

The Institute for Chemical Research, Kyoto.

(1) Taylor, "A treatise on physical chemistry", (1925), p. 1157.

(2) Magnus (*Physik. Z.*, **14** (1913), 5) gave $C_{\text{NaCl}} = 13.33$ between 18° and 763°C.

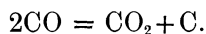
ON THE DECOMPOSITION OF CARBON MONOXIDE IN THE PRESENCE OF REDUCED NICKEL.

(Preliminary Report)

By Shinkichi HORIBA and Taikei RI.

Received December 23, 1927. Published January 28, 1928.

As one of the most simple catalytic reactions, we may cite the decomposition of carbon monoxide in the presence of reduced nickel:



Although many studies of this reaction have been given in the literature, still a more comprehensive investigation of such a simple catalytic reaction is to be desired, for it would, in the writers' opinion, contribute some important materials to facilitate the theoretical studies of contact catalysis, which is one of the most interesting problems in physical chemistry at the present time.

Since this catalytic reaction had been found by Ste.-Claire Deville⁽¹⁾ in 1863, it was studied by many investigators, but their modes of investigation can, in general, be divided into two classes; namely, the first is related to chemical statics (equilibrium), and the other to the kinetics of the reaction. The number of report belonging to the former class is very great,⁽²⁾ since the investigation of the equilibrium of this reaction has much value in technics, while that of the latter class is inconsiderable.⁽³⁾ So far as the present writers know, there is no investigation of this reaction which is simultaneously studied from the two view points of reaction statics and of kinetics. The writers have, therefore, constructed an improved apparatus for the measurement of the reaction velocities as well as of the equilibrium, in the hope of elucidating the relationship that may be established between the reaction statics and the reaction kinetics and also to deduce the mechanism of the nickel catalyst. In the present paper, as a preliminary note, only the description of the apparatus constructed and some results of experiments will be given.

(1) Ste.-Clair Deville, *Compt. rend.*, **56** (1863), 729.

(2) Boudouard, *Ann. chim. phys.*, [7], **24** (1901), 5; Max Mayer, "Habilitationsschrift Karlsruhe," (1908); Read and Wheeler, *J. Chem. Soc.*, **97** (1910), 2181; *ibid.*, **99** (1911), 1140; Arndt and Schraube, Dissertation Charlottenburg (1911); Falcke, *Z. Elektrochem.*, **27** (1921), 268; Jellinek and Dithem, *Z. anorg. allgem. Chem.*, **124** (1922), 203; Falcke and Fischer, *Z. Elektrochem.*, **32** (1926), 194; Falcke, *ibid.*, **33** (1927), 1; Alfred Stansfield, *Trans. Am. Elektrochem. Soc.*, **51** (1927), 5.

(3) Schenk and Zimmermann, *Ber.*, **36** (1903), 1231 & 3663; Smits and Wolff, *Z. physik. Chem.*, **45** (1903), 199; J. Cleminson and H.V.A. Briscoe, *J. Chem. Soc.*, (1926), 2148.

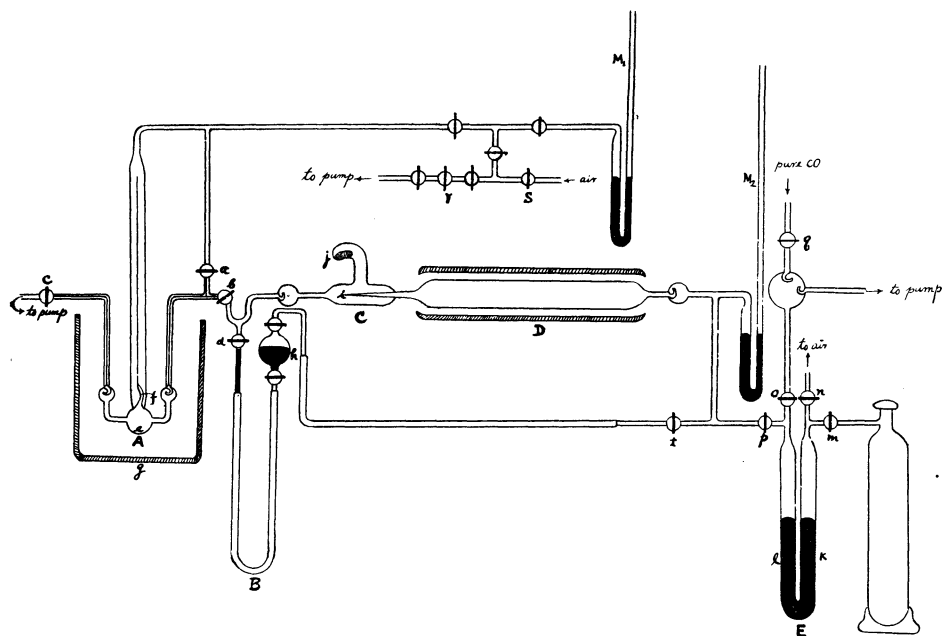


Fig. 1.

Apparatus of the Measurements. The apparatus constructed is mainly divided into five parts, as represented by A, B, C, D and E in Fig. 1. A is the reaction vessel (made of Pyrex glass) provided with a spring manometer *f* and with two capillary tubes which are furnished with cocks *a*, *b* and *c* and when these cocks are closed the internal volume of this reaction vessel is about 30 c.c. The catalyst was placed into the part *e* of the vessel. The cock *b* is a specially made one, 2.4 cm. in diameter and 12 cm. in length, two sides of which were sealed by means of mercury from the atmosphere. In this cock, the least possible modicum of grease was applied for the sake of lubrication on two sides of it, but absolutely none in the middle part of the cock; the employment of such a cock is of vast importance in the present experiment, otherwise a minute trace of grease may enter into the reaction vessel accompanying the stream of carbon monoxide, when the latter was charged into the evacuated vessel A. The bath *g* is made up of a melted mixture of sodium and potassium nitrates in an equimolecular proportion, provided with two glass rods for stirring.

B is that part of the apparatus intended to secure the perfect sealing of the cock *b* to prevent any leaking of gas through the nongreased portion of *b*, and this sealing was performed by shutting up the Y-formed glass tube with mercury, by bringing up the mercury reservoir *h*. To prevent the

contamination of the mercury by the grease, the other cock *d*, which was constructed in the same form as *b*, was employed.

C is the apparatus for charging the reaction vessel with the gas, and it was also used merely to prevent the entering of the grease into the reaction vessel. The glass tube *i* is drawn out at one end into a fine point and sealed, and *j* is a piece of soft iron covered with glass. In charging the reaction vessel with the gas from the preheater D, into which the gas had previously been poured, the soft iron falls on the end of the glass tube *i* by means of a magnet and breaks it: as a consequence the gas streams into the evacuated reaction vessel through the Y-formed tube and cock *b*.

D is the preheater of the reacting gas before it is poured into the reaction vessel, and was used for the purpose of equalizing the temperature of the gas and that of the reaction vessel A; for heating D, an electric furnace was used, and its temperature was measured by a platinum-platinum-rhodium thermocouple.

E is the pump to raise the pressure of the gas in the preheater to the desired amount. Its height is about 90 cm. and was filled with mercury up to the height of 45 cm. For supplying the pressure to this pump a CO₂ bomb was used as shown in the figure.

Materials. The catalyst used was prepared by ignition of pure nickel nitrate Ni(NO₃)₂·6H₂O (Kahlbaum, Co free) in a crucible, subjected to a red heat during one day, and then the NiO thus prepared (about 10 gr.) was introduced into the reaction vessel A and reduced by electrolytic hydrogen (purified) at a temperature of 280°C.

Carbon monoxide was prepared by dropping pure formic acid on heated sulphuric acid at 100°C. and this was purified by passing three bottles each of conc. KOH solution and pyrogallol solution, two bottles of conc. H₂SO₄ and then a P₂O₅ tube, and it was found that the purity of the thus prepared carbon monoxide was 100%.

The Method of the Measurements. The reaction vessel was heated in the nitrate bath *g* at the desired temperature and the whole apparatus was evacuated with a Cenco Hyvac pump, leaving open all the cocks except *m*, *n*, *q* and *s*, until the Geisler tube, which was attached to the pump, showed fluorescence. Then the cocks *c* and *d* were closed and through the cock *q* purified carbon monoxide was introduced into the pump E and preheater D. Next, with the aid of pump E, carbon monoxide was compressed into the preheater, which was heated to the same temperature as the reaction vessel, at the desired pressure. The pressure of D before pouring it into the reaction vessel was read by means of the mercury manometer M₂; from this reading of the pressure, the pressure, which would be exerted by the gas in the reaction vessel after being charged, could be expected. Now the

soft iron piece above mentioned has made fallen and broken the end of the narrow tube *i*, thus the gas streamed into the reaction vessel A. When all the systems had reached an equilibrium of pressure, the cock *d* was opened, then the mercury ran from the reservoir, which was held previously at a suitable height, into the Y-formed tube and sealed this part. The cocks *a*, *b* and *d*, then, were quickly closed, the pressure of the reaction vessel at the initial time being read by the manometer M_1 ; the whole time required in this charging process of the gas was only about 10 seconds. The gas thus enclosed within the reaction vessel of constant volume by the above procedure decomposes to CO_2 and C in the presence of the nickel catalyst. During the progress of the reaction, the pressure change of the reaction vessel is easily indicated by the spring manometer. Adjusting the outer pressure of the spring by means of the cocks *r* and *s* and keeping the pointer of the spring manometer in the zero position, the pressure of the reaction vessel at any time was measured. By reading the pressure from time to time in this way, the decomposition velocity of the gas was determined.

The Experimental Results. The results of the four series of experiments in the vicinity of $230^\circ C.$, applying the same catalyst, were as follows:

TABLE 1.
(at $232.5^\circ C.$)

Time. (min.)	Press. (mm.)	2.303 <i>k</i> (time in min.)
0.00	270.4	
2.42	256.2	0.0204
3.73	243.1	0.0264
5.88	231.0	0.0256
8.23	219.6	0.0249
11.27	207.2	0.0240
12.90	201.7	0.0238
14.18	197.7	0.0238
15.10	194.1	0.0240
17.56	190.6	0.0222
18.63	187.0	0.0224
20.18	183.7	0.0222
22.08	178.5	0.0225
25.69	175.8	0.0204
	(remained constant for about 10 min. and then increased very slowly.)	

TABLE 2.
(at 230°C.)

Time. (min.)	Press. (mm.)	2.303 <i>k</i> (time in min.)
0.00	272.7	
1.00	255.1	0.0607
2.87	242.4	0.0383
4.75	235.4	0.0295
7.00	225.1	0.0268
8.70	221.1	0.0239
9.90	217.3	0.0230
11.63	211.9	0.0222
13.10	207.8	0.0215
14.50	202.1	0.0219
16.95	197.2	0.0207
19.27	192.0	0.0203
21.68	186.4	0.0201
24.30	179.9	0.0204
26.75	174.9	0.0205
30.10	170.6	0.0200
32.72	167.9	0.0195
38.22	162.8	0.0187
(tended to increase; after about 40 min. increased to 178.0 min.)		

TABLE 3.
(at 233.5°C.)

Time. (min.)	Press. (mm.)	2.303 <i>k</i> (time in min.)
0.00	272.0	
1.05	253.9	0.0592
2.53	242.7	0.0423
3.95	232.3	0.0379
5.55	224.7	0.0333
7.18	216.8	0.0312
9.12	209.1	0.0296
11.40	200.1	0.0287
13.43	196.8	0.0260
15.03	190.8	0.0258
16.80	185.6	0.0261
18.88	179.2	0.0264
21.58	174.1	0.0257
23.73	168.6	0.0262
26.72	165.0	0.0252
(tended to increase; after about 40 min. increased to 176.2 mm.)		

TABLE 4.
(at 231.5°C.)

Time. (min.)	Press. (mm.)	2.303 k (time in min.)
0.00	253.3	
1.08	239.1	0.0472
2.40	229.0	0.0385
3.83	221.1	0.0333
5.15	215.1	0.0301
6.90	206.5	0.0290
9.07	199.4	0.0265
11.72	191.0	0.0250
15.20	182.3	0.0235
17.93	177.8	0.0219
20.60	172.3	0.0215
23.82	167.1	0.0209
27.53	162.2	0.0201
31.57	155.8	0.0202
36.95	152.8	0.0185
(remained constant for 8 min.; after 35 min. in- creased to 163.3 mm.)		

The values of k in the third column were obtained by the application of the ordinary monomolecular reaction formula,

$$k = \frac{1}{t} \ln \frac{p_0}{2p_t - p_0},$$

where p_0 and p_t denote the initial pressure and the pressure of time t respectively.

In every experiment, the constancy of the reaction constant, after about 15 minutes, is quite good, and it shows that the decomposition of carbon monoxide is monomolecular. Now what about the rapid decreasing of the pressure in the initial period of the reaction? The writers hold the opinion that it might be mainly due to the adsorption of carbon monoxide on reduced nickel. In fact, if we take the adsorption formula⁽¹⁾

$$k' = \frac{1}{t} \ln \frac{A}{A - x},$$

where A denotes the total amount adsorbed when equilibrium is attained, and x the amount adsorbed in the time t , we have approximate constant values about the adsorption velocity constant k' , after choosing suitable values in A from the data of the above experiments, for examples:

(1) Blythswood and Allen, *Phil. Mag.*, 10 (1905), 497.

TABLE 5.

Time. (min.)	$x (=p_0-p_t)$	k' (time in min.)
(from Table 2)		
0.00	0	0.1245
1.00	17.6	0.0848
2.87	30.3	0.0688
4.75	37.3	0.0695
7.00	47.6	0.0656
8.70	51.6	0.0676
9.90	55.4	0.0738
11.63	60.8	0.0834
13.10	64.9	
where $A=272.7-202.1=70.6$ mm.		
(from Table 4)		
0.00	0.	0.0893
1.08	14.2	0.0758
2.40	24.3	0.0686
3.83	32.2	0.0650
5.15	38.2	0.0732
6.90	46.8	0.0682
9.07	53.9	0.0780
11.72	62.3	
where $A=253.3-182.3=71.0$ mm.		

We may say, it is not at all improbable that reduced nickel has such degree of adsorptive power towards carbon monoxide even at that temperature, if we noticed remarkable adsorptive power of it at low temperature. About the latter, the writers have already carried out experiments, which will be published in the near future.

As seen in the present experiments, the decomposition of carbon monoxide is not complete at those temperatures. This result contradicts the prediction from the studies of chemical statics of this reaction, which had been carried out by many investigators, and it requires further studies to clear up reason for this.

As shown in the tables 1-4, in every experiment, the pressure at the end of the reaction tends to increase, even if this velocity of increasing pressure is exceedingly small compared to that of the decomposition of the gas. The cause of this increasing of the pressure is not yet clear. The

writers hold the opinion that it depends upon the reaction between carbon dioxide or carbon monoxide and hydrogen; the latter would be brought into the system by the adsorption of the catalyst when it was prepared. The experiments in connection with this problem are now proceeding.

Even the some difficulties as above described in this reaction still remain, it is quite certain that the decomposition of carbon monoxide in the presence of a nickel catalyst is monomolecular and it may, therefore; be explained by Langmuir's theory of heterogeneous reaction. But this theoretical discussion will be left until a more comprehensive examination is concluded.

Summary.

An improved apparatus for the investigation of contact catalysis was described.

The decomposition of carbon monoxide in the presence of reduced nickel is a monomolecular reaction in the vicinity of 230°C.

December 1927.

The Institute for Chemical Research,
Kyoto.

ON THE DEVIATION OF GASEOUS MIXTURES FROM DALTON'S
LAW OF PARTIAL PRESSURES DUE TO CHEMICAL CAUSES.
III. HYDROGEN CHLORIDE AND METHYL ALCOHOL.

By Jitaro SHIDEI.

Received December 23, 1927. Published January 28, 1928.

Introduction. In the previous papers of this series⁽¹⁾ the action of hydrogen chloride on methyl ether and on water was described. It was shown that the volume contraction or pressure diminution which will take place when the two component gases are mixed was due to the addition reaction prevailing between them, and this reaction was ascribed to the ability of the oxygen atom which is contained in both methyl ether and water to act as quadrivalent.

Methyl alcohol is similar in its constitution to methyl ether and water and contains the oxygen atom above mentioned. The evidence that with

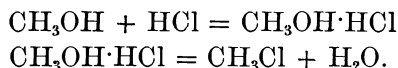
(1) Previous papers of this series have appeared as follows:—

I, *Memoirs of Coll. Sci. Kyoto Imp. Univ.*, Series A, IX, No. 2, (1925), p. 98.

II, The Sexagint (being a collection of papers dedicated to Prof. Yukichi Osaka by his pupils in celebration of his 60th Birthday), (1927), p. 143.

hydrogen chloride it forms a similar addition compound was shown briefly in the second paper of this series. In methyl ether and water molecules, however, the similar radicals are attached to the oxygen atom, while in methyl alcohol the two are different from each other. Hence, though methyl alcohol is able to form the addition compound with hydrogen chloride, the kind of the reaction may be in its nature somewhat different from those with methyl ether and water.

Carter and Butler⁽¹⁾ proved the formation of methyl chloride from the mixtures of dry methyl alcohol and dry hydrogen chloride at 18°C., but no exact quantitative study of the reaction seems to have been published. The formation of methyl chloride may be illustrated by the addition reaction between the components and the subsequent decomposition of the resulting substance into methyl chloride and water, as may be shown by the expressions:—



The formation of the halogen alkyl has also been considered by some investigators to take place in this way. Thus, from the results of the reactions between alcohols and halogen acids, Norris and Mulliken⁽²⁾ came to the conclusion: "It seems probable . . . the reaction between an alcohol and a halogen acid consists in the addition of the two compounds and the subsequent elimination of water. The ease with which the two separate steps occur determines whether reaction takes place or not under the condition used."

The object of the experiments herein described is to obtain some information as to the addition reaction between methyl alcohol and hydrogen chloride in the gaseous state under the influence of the second reaction, if that second reaction takes place.

Experimental Part.

Materials. *Methyl alcohol*.—Methyl alcohol of a high grade of Kahlbaum was employed. This was distilled first with lime and then with anhydrous copper sulphate three times respectively. The methyl alcohol thus dried was kept in a glass bottle, tightly sealed. Through all the experiments, this same material was used.

In the case of the measurements of its pressures it was sealed in a small tube of Pyrex glass in the same manner as was previously adopted in the case of the hydrochloric acid.

(1) *J. Chem. Soc.*, **125** (1924) 963.

(2) *J. Am. Chem. Soc.*, **42** (1920), 2093.

Hydrogen chloride:—It was prepared by the usual method of adding conc. sulphuric acid to conc. hydrochloric acid. This was thoroughly dried in a way which will be described later.

The weights of the hydrogen chloride used in the pressure measurements could not be determined directly. Hence, they were found by calculation from its pressures as measured.

Apparatus and Experimental Procedure. For the measurements of the gaseous pressures, the apparatus which had previously been used in the case of the system $\text{HCl}-\text{H}_2\text{O}$ was here employed again. The general construction of the apparatus to conduct hydrogen chloride from its generator into the apparatus for the measurements of the pressures, Q , is shown in Fig. 1, which is not drawn to scale.

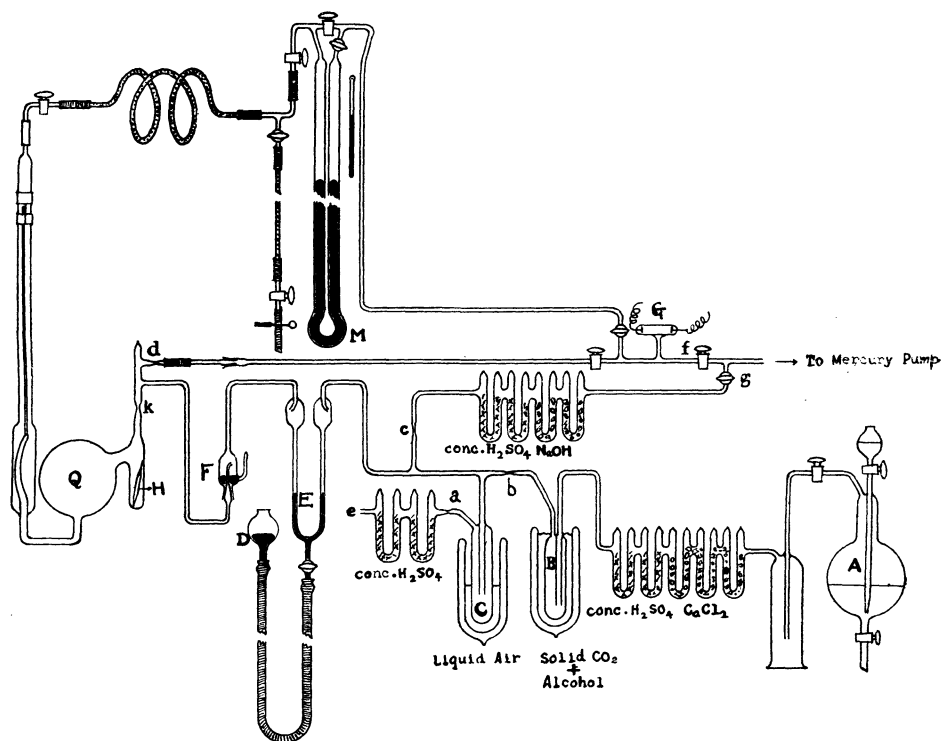


Fig. 1.

The gas generator and the conducting tubes were all made of ordinary glass. The conducting tubes were connected to the measuring apparatus, which was made of Pyrex glass, by the ground joint, F . The wax for sealing the joint was prevented from direct contact with the gas by being covered with a layer of pure dry mercury. The U-tube, E , with pure dry mercury was employed to cut off the direct communication of the measuring

apparatus with the reservoir of the hydrogen chloride. Therefore, the passage of the gas from its generator to the measuring apparatus was constructed entirely of glass, so that the gas could never come in contact with any materials but glass and mercury.

Hydrogen chloride from its generator, A, was dried by being passed through CaCl_2 and conc. H_2SO_4 tubes successively and then through the cooling tube, B, which was immersed in a mixture of solid carbon dioxide and alcohol in a Dewar flask. The gas thus dried was at first driven out through the exit, e, until the air in the generator was nearly swept out with the gas, when the conducting tube was sealed off at the constriction, a. The cooling tube, C, which served as the reservoir of the hydrogen chloride, was then immersed in liquid air. When a suitable quantity of the gas was solidified in the tube, the tube was sealed off at b.

The exhaustion of the measuring apparatus and the reservoir of the hydrogen chloride was at first alternately carried out by means of a mercury pump, the cocks f and g being opened alternately, not to allow the gas to enter the measuring apparatus. In order to remove the foreign gases which may have been occluded in the solid hydrogen chloride, the reservoir when fairly well exhausted was for a while detached from the liquid air. Meanwhile the pumping was continued, the cock, g, alone being now opened. After this operation the reservoir was again immersed in the liquid air and the pumping was continued until a vacuum was reached, the degree of which was such that the Geissler tube, G, was covered with fluorescence, when the conducting tube was sealed off at c. Before sealing off the tube, d, the measuring apparatus and the reservoir were once more subjected to the pumping, being now allowed to communicate with each other by lowering the level bulb, D, suitably. Finally, the hydrogen chloride was allowed to evaporate and the required amount of it was introduced into the measuring apparatus by suitably adjusting its cooling. The apparatus was sealed off at k.

In the case of measuring the pressures of the mixtures, before the mixing of the two materials, the pressures of the hydrogen chloride alone were measured at 50°C ., higher temperatures being avoided lest the sample tube of the methyl alcohol, H, should be broken by thermal expansion of the material.

The methods of measuring the pressures and also of mixing the two materials were the same as employed in the case of the study of the system $\text{HCl}-\text{H}_2\text{O}$.

Results of the Experiments. For the purpose of carrying out the theoretical calculation of the partial pressures of each component gas, which will be given later, the pressures of the single gases were first measured. The results of the experiments with the gaseous methyl alcohol are summarized in Table 1. The amounts of methyl alcohol used ranged from 0.15508 to 0.5565 gr. The volume of the reaction vessel was about 240 c.c., but it varied somewhat in every experiment. Therefore, the amounts of the sample used were converted to the weight per litre. These are given in column 1. The pressures of the hydrogen chloride observed are given in column 2 of Table 2. The results of the experiments with the mixtures are contained in Table 3.

TABLE 1.—Methyl alcohol.

A. Temperature: 70°C.

Weight (per litre) gr.	Pressure mm.
0.23129	154.54
0.26690	177.35
0.29574	197.15
0.35129	233.85
0.45679	302.74
0.48005	319.42
0.64458	426.40

B. Temperature: 90°C.

Weight (per litre) gr.	Pressure mm.
0.23124	163.87
0.26385	187.45
0.29568	208.86
0.35122	248.00
0.45670	321.42
0.47995	339.07
0.64445	453.90

C. Temperature: 110°C.

Weight (per litre) gr.	Pressure mm.
0.23119	172.67
0.26679	198.03
0.29562	220.56
0.35115	261.95
0.45661	339.84
0.47986	358.16
0.64432	480.01

D. Temperature: 130°C.

Weight (per litre) gr.	Pressure mm.
0.23115	181.41
0.26674	208.54
0.29557	231.82
0.35108	276.64
0.45652	357.97
0.47976	377.99
0.64420	506.29

TABLE 2.—Hydrogen chloride.

A. m (calc.)=0.0024904;
 Volume of the reaction vessel⁽¹⁾
 at 25°C.=241.466 c.c.

Temp. °C.	Pressure obs. mm.	Pressure calc. mm.
50	207.57	207.57
70	220.47	220.41
90	233.20	233.23
110	246.00	246.06
130	259.10	258.87

B. m (calc.)=0.0032072;
 Volume of the reaction vessel
 at 25°C.=240.847 c.c.

Temp. °C.	Pressure obs. mm.	Pressure calc. mm.
50	267.99	267.99
70	284.47	284.51
90	300.95	301.07
110	317.59	317.63
130	333.97	334.18

C. m (calc.)=0.0040254;
 Volume of the reaction vessel
 at 25°C.=240.145 c.c.

Temp. °C.	Pressure obs. mm.	Pressure calc. mm.
50	337.14	337.14
70	358.10	358.01
90	378.82	378.88
110	399.77	399.73
130	421.29	420.57

(1) The change of the volume of the reaction vessel with temperature was calculated from the linear expansion coefficient 0.0000031 of Pyrex glass.

TABLE 3.

Experiment 1.

Weight of CH_3OH taken = 0.06256 gr. (= 0.0019527 mol);

Pressure of HCl at 50°C . = 193.50 mm.;

Mol of HCl calculated = 0.0023201;

Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 241.411 c.c.⁽¹⁾ [−0.078].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.25903	172.80	205.39	378.2	375.9	2.3
90	0.25897	183.15	217.35	400.5	398.8	1.7
110	0.25892	193.20	229.29	422.5	421.2	1.3

Experiment 2.

Weight of CH_3OH taken = 0.05477 gr. (= 0.0017096 mol);

Pressure of HCl at 50°C . = 331.64 mm.;

Mol of HCl calculated = 0.0039725;

Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 240.995 c.c. [−0.068].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.22716	151.90	352.07	504.0	500.49	3.5
90	0.22712	160.85	372.59	533.4	530.70	2.7
110	0.22707	169.70	393.04	562.7	560.75	2.0
130	0.22703	178.10	414.20	592.3	590.80	1.5

- (1) The volumes of the reaction vessel at 25°C . given in this table are distinguished from those in Table 2 in showing the volume of the vessel minus the volume of the glass of the sample tube. For the calculation of the mols of hydrogen chloride from its data at 50°C . the volume of the methyl alcohol sealed in the tubes, which is given in the brackets, was again subtracted from that of the vessel just mentioned at 50°C .

TABLE 3. (continued).

Experiment 3.

Weight of CH_3OH taken = 0.07178 gr. (= 0.0022405 mol);Pressure of HCl at 50°C . = 207.31 mm.;Mol of HCl calculated = 0.0024710;Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 239.979 c.c. [-0.090].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.29898	198.90	220.55	419.5	416.6	2.9
90	0.29892	211.20	232.85	444.1	441.8	2.3
110	0.29886	222.90	245.65	468.6	467.0	1.6
130	0.29380	234.34	258.85	493.2	492.0	1.2

Experiment 4.

Weight of CH_3OH taken = 0.07147 gr. (= 0.0022309 mol);Pressure of HCl at 50°C . = 113.33 mm.;Mol of HCl calculated = 0.0013508;Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 240.096 c.c. [-0.089].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.29754	198.1	120.29	318.4	316.8	1.6
90	0.29748	210.2	127.26	337.5	336.3	1.2
110	0.29742	221.9	134.22	356.1	355.2	0.9
130	0.29736	233.3	141.39	374.7	374.0	0.7

Experiment 5.

Weight of CH_3OH taken = 0.12032 gr. (= 0.0037557 mol);Pressure of HCl at 50°C . = 362.81 mm.;Mol of HCl calculated = 0.0043397;Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 240.698 c.c. [-0.150].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
90	0.49955	351.7	407.49	759.20	753.29	5.9
110	0.49946	371.9	429.92	801.80	797.40	4.4
130	0.49936	391.9	452.90	844.80	841.60	3.2

TABLE 3. (continued).

Experiment 6.

Weight of CH_3OH taken = 0.14140 gr. (= 0.0044137 mol);Pressure of HCl at 50°C . = 227.50 mm.;Mol of HCl calculated = 0.0027141;Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 240.260 c.c. [- 0.177].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
90	0.58815	414.0	255.44	669.4	664.40	5.0
110	0.58803	438.1	269.49	707.6	703.60	4.0
130	0.58791	461.9	283.92	745.8	742.47	3.3

Experiment 7.

Weight of CH_3OH taken = 0.10400 gr. (= 0.0032463 mol);Pressure of HCl at 50°C . = 214.86 mm.;Mol of HCl calculated = 0.0025546;Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 239.408 c.c. [- 0.130].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
90	0.43412	305.5	241.29	546.8	543.8	3.0
110	0.43404	323.0	254.80	577.8	575.5	2.3
130	0.43395	340.2	268.20	608.4	606.6	1.8

Experiment 8.

Weight of CH_3OH taken = 0.08413 gr. (= 0.0026260 mol);Pressure of HCl at 50°C . = 316.41 mm.;Mol of HCl calculated = 0.0037793;Volume of reaction vessel (less vol. of glass tube)
at 25°C . = 240.369 c.c. [- 0.105].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.34985	232.4	335.84	568.2	563.3	4.9
90	0.34978	246.9	355.41	602.3	598.4	3.9
110	0.34971	260.6	374.97	635.6	632.7	2.9
130	0.34964	274.1	395.00	669.1	666.9	2.2

TABLE 3. (continued).

Experiment 9.

Weight of CH_3OH taken = 0.09465 gr. (= 0.0029544 mol);Pressure of HCl at 50°C . = 156.80 mm.;Mol of HCl calculated = 0.0018737;

Volume of reaction vessel (less vol. of glass tube)

at 25°C . = 240.676 c.c. [-0.118].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.39309	260.5	163.40	426.9	424.10	2.8
90	0.39301	276.9	176.00	452.9	450.70	2.2
110	0.39293	292.6	185.76	478.4	476.79	1.6
130	0.39286	308.2	195.70	503.9	502.67	1.2

Experiment 10.

Weight of CH_3OH taken = 0.07716 gr. (= 0.0024085 mol);Pressure of HCl at 50°C . = 199.57 mm.;Mol of HCl calculated = 0.0023767;

Volume of reaction vessel (less vol. of glass tube)

at 25°C . = 239.777 c.c. [-0.096].

Temp. $^\circ\text{C}$.	Weight of CH_3OH (per litre) gr.	$p_{\text{CH}_3\text{OH}}$ mm.	p_{HCl} mm.	P calc. mm.	P obs. mm.	ΔP mm.
70	0.32165	214.0	211.80	425.8	422.9	2.9
90	0.32159	227.1	224.16	451.3	449.1	2.2
110	0.32153	239.7	236.48	476.2	474.6	1.6
130	0.32146	252.2	249.20	501.4	500.2	1.2

Theoretical Part.

Calculation of the Pressures of the Single Gases. *Methyl alcohol* :—

The pressures of the gaseous methyl alcohol given in Table 1 are shown plotted against weight in Fig. 2. It will be seen that though the values of the pressures observed differ somewhat from those of Ramsay and Steele⁽¹⁾ they change regularly with the weights taken and give a series of straight

(1) *Z. physik. Chem.*, **44** (1903), 348.

lines which nearly pass through the origin of the co-ordinates. No irregularities in the pressure change are found through the whole series. Hence, the partial pressures which the methyl alcohol would exert if it behaved

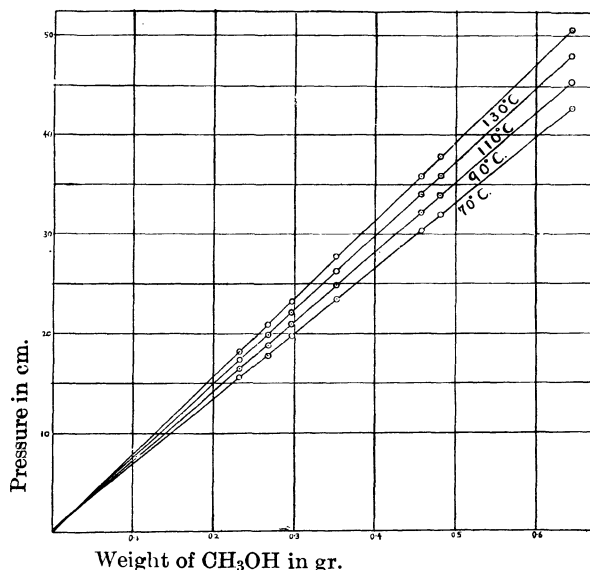


Fig. 2.

independently of the other component in the gaseous mixtures may be found graphically with sufficient accuracy by means of the curves in Fig. 2. The partial pressures $p_{\text{CH}_3\text{OH}}$ shown in Table 3 are those which were found in this way, the weights per litre being employed, to which the weights of the substance actually taken were converted.

Hydrogen chloride :—In the second paper of this series the pressures of hydrogen chloride were calculated by means of van der Waals' equation :—

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT, \dots\dots\dots(1)$$

changes of a and b with temperature being allowed for by van Laar's equations for their temperature coefficients :—

$$\left. \begin{aligned} a_T &= a_e e^{\alpha \left(\frac{1}{RT} - \frac{1}{RT_e} \right)} \\ b_T &= b_e e^{\alpha \left(\frac{1}{RT} - \frac{1}{RT_e} \right)} \end{aligned} \right\} \dots\dots\dots(2)$$

As was shown previously, if p is measured in atmospheres and v in the volume which the quantity of gas concerned would occupy in the normal state, then the value of R is equal to $1/273.09$.

The calculated values of a and b of hydrogen chloride at 323.09° and 343.09°K. respectively are as follows :—

$$\begin{aligned} a_{323.09} &= 7444 \times 10^{-6}; & b_{323.09} &= 1826 \times 10^{-6}; \\ a_{343.09} &= 7021 \times 10^{-6}; & b_{343.09} &= 1722 \times 10^{-6}. \end{aligned}$$

The values above 343.09°K. are given in the second paper.

For m mols of the gas, Equation (1) may be written in the following form :—

$$\left(p + \frac{a}{\frac{v^2}{(22412 m)^2}} \right) \left(\frac{v}{22412 m} - b \right) = RT,$$

or

$$\left(p + \frac{a}{v'^2} \right) (v' - b) = RT, \dots\dots\dots(1a)$$

where $v' = v/22412 m$.

Solving Equation (1a) for v' , we obtain

$$\begin{aligned} v' &= \frac{v}{22412 m} \\ &= \left[\frac{1}{27} \left(b + \frac{RT}{p} \right)^3 + \frac{a}{6p} \left(2b - \frac{RT}{p} \right) + \left\{ \frac{1}{4} \left[\frac{2}{27} \left(b + \frac{RT}{p} \right)^3 \right. \right. \right. \\ &\quad \left. \left. + \frac{a}{3p} \left(2b - \frac{RT}{p} \right) \right]^2 + \frac{1}{27} \left[\frac{a}{p} - \frac{1}{3} \left(b + \frac{RT}{p} \right)^2 \right]^3 \right\}^{\frac{1}{3}} \right]^{\frac{1}{3}} + \left[\frac{1}{27} \left(b + \frac{RT}{p} \right)^3 \right. \\ &\quad \left. + \frac{a}{6p} \left(2b - \frac{RT}{p} \right) - \left\{ \frac{1}{4} \left[\frac{2}{27} \left(b + \frac{RT}{p} \right)^3 + \frac{a}{3p} \left(2b - \frac{RT}{p} \right) \right]^2 \right. \right. \\ &\quad \left. \left. + \frac{1}{27} \left[\frac{a}{p} - \frac{1}{3} \left(b + \frac{RT}{p} \right)^2 \right]^3 \right\}^{\frac{1}{3}} \right]^{\frac{1}{3}} + \frac{1}{3} \left(b + \frac{RT}{p} \right), \\ &\dots\dots\dots(3) \end{aligned}$$

for the real root. Then, substituting the experimental values in Equation (3), mols of hydrogen chloride can be calculated. For the purpose of the calculation, the experimental data at 50°C. given in Table 2 were employed. The results of the calculation are shown in the same table. The last column of the table contains the pressures of the hydrogen chloride at the temperatures given in column 1 calculated by means of Equation (1) employing each value of m above obtained.

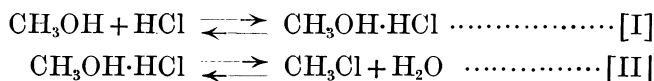
From Table 2, it will be seen that up to 110°C., the theoretical and experimental values of the pressures are in good agreement within 0.1 mm. Hence, up to 110°C., Equation (1) will be available with sufficient accuracy

within 0.1 mm. for the calculation of the partial pressures which the hydrogen chloride would exert if it behaved independently of the other component in the mixtures. At 130°C., a discrepancy of 0.2 to 0.7 mm. may be found, so that in this case the corrections due to the discrepancy must be applied to the theoretical values.

The partial pressures of the hydrogen chloride in the mixtures thus calculated are given under p_{HCl} in Table 3. In this table, the mols of the hydrogen chloride were calculated from the experimental data at 50°C. given in the same table.

Discussion of the Results. A comparison of the values of the total pressures calculated by Dalton's law with those observed shows evidently the occurrence of pressure diminution by the mixing of the two gases. The last column of Table 3 contains the pressure diminutions.

To elucidate the cause of the diminution from the chemical standpoint, at least the following two reactions must be taken into consideration:—



Reaction [I], as considered by Norris and Mulliken, is the primary reaction of the ester formation of halogen acid. The addition compound thus formed will then be decomposed into methyl chloride and water ultimately. On the other hand, it may be possible that methyl chloride undergoes hydrolytic decomposition, however trivial in amount, although it is generally believed that such decomposition, if it takes place at all, must be accomplished with great difficulty. In this case, however, it is probable that the methyl chloride and water will also primarily make the addition reaction and will again produce $\text{CH}_3\text{OH}\cdot\text{HCl}$. Therefore, the second reaction of the ester formation will be expressed by the balanced action as above shown.

If K_1 and K_2 be the equilibrium constants of reactions [I] and [II] at constant volume respectively, then, as usual, they are given by the expressions—

$$K_1 = \frac{c_{\text{CH}_3\text{OH}} c_{\text{HCl}}}{c_{\text{CH}_3\text{OH}\cdot\text{HCl}}} \dots\dots\dots (4)$$

$$K_2 = \frac{c_{\text{CH}_3\text{OH}\cdot\text{HCl}}}{c_{\text{CH}_3\text{Cl}} c_{\text{H}_2\text{O}}}, \dots\dots\dots (5)$$

in which c with the suffixes are concentration terms at equilibrium.

Let m_1 and m_2 be the mols of methyl alcohol and hydrogen chloride initially taken respectively; α the fraction of the methyl alcohol transformed at equilibrium; γ the dissociation degree of the addition compound at equilibrium; v the volume of the reaction vessel measured in c.c. Then the equilibrium constants can be represented by the expressions—

$$K_1 = \frac{(m_1 - m_1\alpha)(m_2 - m_1\alpha)}{v m_1\alpha (1-\gamma)} = \frac{(1-\alpha)(m_2 - m_1\alpha)}{v \alpha (1-\gamma)}, \dots\dots(4a)$$

$$K_2 = \frac{v m_1\alpha (1-\gamma)}{m_1^2 \alpha^2 \gamma^2} = \frac{v (1-\gamma)}{m_1 \alpha \gamma^2} \dots\dots\dots(5a)$$

If P is the total pressure of the system at equilibrium in which the existence of the two reactions is assumed, and if P' is that which the mixture would exert if the component gases behaved independently of each other, then

$$\frac{P}{P'} = \frac{m_1(1-\alpha) + m_2 - m_1\alpha + m_1\alpha(1-\gamma) + 2 m_1\alpha \gamma}{m_1 + m_2}$$

or

$$= \frac{m_1 + m_2 - m_1\alpha(1-\gamma)}{m_1 + m_2},$$

wherefore

$$\alpha = \frac{(m_1 + m_2)(1 - P/P')}{m_1(1-\gamma)} \dots\dots\dots(6)$$

Substituting α thus found in Equation (4a), there is obtained

$$K_1 = \frac{(m'P/P' - m_2 - m_1\gamma)(m'P/P' - m_1 - m_2\gamma)}{v m' (1 - P/P') (1-\gamma)^2}, \dots\dots\dots(7)$$

where $m' = m_1 + m_2$.

For very small magnitudes of γ , Equation (7) is reduced to that which was obtained in the case of the system $\text{HCl}-\text{H}_2\text{O}$ and it will approximately regulate the equilibrium in the absence of the second reaction. The values of K_1' given in Table 4 are those which were calculated by Equation (7) in which γ was put at zero. Column 2 and 3 of the table contain the mols of the methyl alcohol and the hydrogen chloride initially taken respectively, column 5 contains the ratios of the larger value to the smaller one in m_1 and m_2 and column 6 the substances which were taken in excess of the other component.

TABLE 4.

Exp. No.	$m_1 \times 10^7$	$m_2 \times 10^7$	$m' \times 10^7$	Ratio	Subst. in excess	K'_1 (70°C.) $\times 10^6$	K'_1 (90°C.) $\times 10^6$	K'_1 (110°C.) $\times 10^6$	K'_1 (130°C.) $\times 10^6$
10	24085	23767	47851	1.01	CH ₃ OH	712	1003	1466	2063
3	22405	24710	47115	1.10	HCl	689	985	1413	1991
5	37557	43397	80954	1.16	HCl	—	1038	1489	2172
1	19527	23201	42728	1.19	HCl	704	1016	1403	—
7	32463	25346	58008	1.27	CH ₃ OH	—	1063	1475	1992
8	26260	37793	64053	1.44	HCl	721	968	1385	1932
9	29544	18737	48281	1.58	CH ₃ OH	706	960	1398	1936
6	44137	27141	71278	1.63	CH ₃ OH	—	906	1207	1550 ⁽¹⁾
4	22309	13508	35817	1.65	CH ₃ OH	682	970	1371	1859
2	17096	39725	56821	2.32	HCl	688	956	1407	1931
Mean						700	995	1424	1985
Deviation (%)						1.71	3.08	2.49	3.53

The deviation of each value of K'_1 from its mean value is small. But, there may be pointed out some peculiarities in the deviation. Thus, within experimental error the values of K'_1 appear to increase, on the one hand, with the approaching of the values of m_1 and m_2 to each other so far as the total mols are constant, and on the other, with the increase of the total mols. The deviation must certainly be caused by neglecting the terms containing γ . The values of γ change with the proportions in which the two gases are mixed, and it will easily be shown that in case of a given total of mols of the two gases initially taken γ attains a maximum value when $m_1 = m_2^{(2)}$.

In order to test the effect of the terms containing γ upon the values of K_1 several values of γ were tried. The results of the calculation show that the deviation of each value of K_1 from its mean value becomes smaller with the increase of the maximum values of γ and then seems to become again greater. Table 5 gives the results of only three cases in which the maximum values assigned to γ are 0.7, 0.8 and 0.9 at 90°C. respectively. Each value of γ used in the calculation is put in brackets below the respective figure for K_1 .

(1) The results of Exp. 6 are not in harmony with the others. Hence they are omitted from the calculation of the mean values of K'_1 .

(2) Combining Equation (4a) with (5a), there is obtained

$$K_1 = \frac{[K_2 m_1 \gamma^2 - v(1-\gamma)][K_2 m_2 \gamma^2 - v(1-\gamma)]}{K_2 v^2 \gamma^2 (1-\gamma)^2} \dots\dots\dots (8)$$

Providing $m' = m_1 + m_2 = \text{const.}$, $\frac{d\gamma}{dm_1}$ and $\frac{d^2\gamma}{dm_1^2}$ will be deduced from Equation (8). Then

it can be proved that $\frac{d\gamma}{dm_1}$ vanishes when $m_1 = m'/2$ and that for this value of m_1 , $\frac{d^2\gamma}{dm_1^2}$ is negative.

TABLE 5.

1. Maximum value of $\gamma = 0.72$ at 90°C .

Exp. No.	K_1 (70°C .) $\times 10^6$	K_1 (90°C .) $\times 10^6$	K_1 (110°C .) $\times 10^6$	K_1 (130°C .) $\times 10^6$
10	667 (0.70)	953 (0.72)	1407 (0.75)	1993 (0.78)
3	644 (0.70)	932 (0.72)	1355 (0.75)	1925 (0.78)
5	—	963 (0.70)	1405 (0.72)	2073 (0.75)
1	668 (0.68)	976 (0.70)	1366 (0.72)	—
7	—	1013 (0.68)	1419 (0.70)	1928 (0.73)
8	673 (0.65)	916 (0.67)	1324 (0.70)	1861 (0.73)
9	670 (0.65)	920 (0.67)	1352 (0.70)	1885 (0.72)
4	662 (0.60)	946 (0.62)	1347 (0.65)	1834 (0.67)
2	654 (0.60)	918 (0.62)	1365 (0.64)	1885 (0.67)
Mean	663	949	1371	1923
Deviation (%)	1.19	2.60	1.90	2.95

2. Maximum value of $\gamma = 0.8$ at 90°C .

Exp. No.	K_1 (70°C .) $\times 10^6$	K_1 (90°C .) $\times 10^6$	K_1 (110°C .) $\times 10^6$	K_1 (130°C .) $\times 10^6$
10	644 (0.78)	925 (0.80)	1377 (0.82)	1952 (0.85)
3	622 (0.78)	904 (0.80)	1326 (0.82)	1882 (0.85)
5	—	911 (0.80)	1342 (0.82)	1987 (0.85)
1	650 (0.76)	955 (0.78)	1339 (0.80)	—
7	—	980 (0.78)	1380 (0.80)	1877 (0.83)
8	640 (0.76)	877 (0.78)	1281 (0.80)	1812 (0.82)
9	648 (0.75)	895 (0.77)	1324 (0.79)	1851 (0.81)
4	643 (0.73)	927 (0.75)	1322 (0.77)	1800 (0.80)
2	635 (0.70)	902 (0.70)	1347 (0.72)	1863 (0.75)
Mean	640	920	1338	1878
Deviation (%)	1.07	2.63	1.61	2.49

TABLE 5. (continued).

3. Maximum value of $\gamma = 0.9$ at 90°C .

Exp. No.	K_1 ($70^\circ\text{C}.$) $\times 10^6$	K_1 ($90^\circ\text{C}.$) $\times 10^6$	K_1 ($110^\circ\text{C}.$) $\times 10^6$	K_1 ($130^\circ\text{C}.$) $\times 10^6$
10	575 (0.88)	833 (0.90)	1247 (0.92)	1703 (0.95)
3	554 (0.88)	808 (0.90)	1198 (0.92)	1638 (0.95)
5	—	763 (0.90)	1132 (0.92)	1752 (0.93)
1	601 (0.86)	892 (0.88)	1255 (0.90)	—
7	—	921 (0.86)	1304 (0.88)	1782 (0.90)
8	580 (0.85)	800 (0.87)	1179 (0.89)	1701 (0.90)
9	606 (0.84)	842 (0.86)	1255 (0.88)	1760 (0.90)
4	612 (0.83)	888 (0.85)	1273 (0.87)	1741 (0.89)
2	608 (0.78)	864 (0.80)	1302 (0.82)	1811 (0.84)
Mean	591	846	1238	1736
Deviation (%)	3.07	4.79	3.71	2.39

From the table it will be seen that the deviation at all the temperatures studied is minimum when the maximum value assigned to γ is 0.8 or so at 90°C . If this value of γ be taken as its most probable value, then the values of α will be found to be between about 0.03 to 0.08 at 90°C . in the range of the experiments given above. But the pressure diminution observed here is very small and the influence of the terms given above upon the values of K_1 is not remarkable unless the γ values should be very large as above shown. Then, whether these values of α be really the true values or not must be ascertained by direct experiment. It is hoped, therefore, to obtain further experimental data on this point.

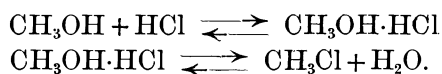
Summary.

1. The gaseous pressures of methyl alcohol of several amounts have been measured at temperatures ranging from 70° to 130°C . It is shown that the pressures measured when plotted against the weights contained in a litre, to which the weights actually taken were converted, give a series of excellent straight lines which nearly pass through the origin of the co-ordinates.

2. The pressures of gaseous hydrogen chloride have been measured over the temperature range, 50° to 130°C . These are shown to be in good

agreement with those which are calculated by van der Waals' equation, changes of his constants with temperature being allowed for by van Laar's equations.

3. Measurements have been carried out of the deviation from Dalton's law at temperatures between 70° and 130°C. in mixtures of several proportions of hydrogen chloride and methyl alcohol. The deviation is discussed from the assumption of the existence of the two reactions:—



The author wishes to express his thanks to Prof. S. Horiba for his kind advice.

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ON THE OXIDATION OF STANNOUS HYDROXIDE IN SODIUM CARBONATE SOLUTION BY MEANS OF AIR.

By Susumu MIYAMOTO.

Received November 26, 1927. Published February 28, 1928.

Introduction. As was described in the previous paper,⁽¹⁾ the oxidation velocity of stannous hydroxide by means of air increases with the increase of the concentration of sodium hydroxide until it attains the dissolution velocity of air into the solution. The increase may be due to the formation of sodium stannite, which dissolves in the solution. The oxidation velocity of stannous hydroxide in sodium carbonate solution can be expected to be very small, as it is almost insoluble in sodium carbonate solution. The present research was carried out to ascertain this idea and as an example of heterogeneous reaction.

Experimental. The experimental procedure was quite the same as that described in the previous paper.⁽²⁾ In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, which is equivalent to the quantity of stannous hydroxide; k was calculated by $k = \frac{1}{t} (v_0 - v)$, v_0 being the value of v at $t = 0$ and $v_{calc.}$ was obtained by $v_{calc.} = v_0 - kt$, using the mean value of k .

TABLE 1.
Temp. = 20° C. Air = 7.78 litres per hour.

$C_{Na_2CO_3}$ normal.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0155	0	9.52	—	—
	120	8.93	8.80	0.00492
	0	12.23	—	—
	150	11.36	12.33	0.00580
	0	12.84	—	—
	120	12.11	12.12	0.00608
	160	11.98	11.88	0.00538
	0	19.27	—	—
	120	18.43	18.55	0.00700
	160	18.19	18.31	0.00675
	0	19.35	—	—
	150	18.44	18.45	0.00607
				mean: 0.00600

(1) S. Miyamoto, this journal, 2 (1927), 155; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 189.

(2) Ibid.

TABLE 1. (Continued.)

$C_{Na_2CO_3}$ normal.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0905	0	10.76	—	—
	120	9.91	9.93	0.00708
	160	9.68	9.66	0.00675
	0	11.52	—	—
	120	10.74	10.69	0.00650
	0	12.23	—	—
	150	11.27	11.19	0.00640
	0	18.00	—	—
	120	17.09	17.13	0.00758
	160	16.87	16.90	0.00706
				mean: 0.00690
0.1655	0	9.43	—	—
	120	8.44	8.51	0.00825
	160	8.21	8.20	0.00763
	0	12.05	—	—
	150	11.01	10.90	0.00693
	0	12.52	—	—
	120	11.61	11.60	0.00758
	160	11.23	11.29	0.00806
	0	17.78	—	—
	120	16.80	16.86	0.00817
	160	16.66	16.55	0.00700
				mean: 0.00766
0.2780	0	11.93	—	—
	120	11.00	11.10	0.00775
	160	10.82	10.82	0.00694
	0	12.31	—	—
	150	11.37	11.27	0.00627
	0	12.87	—	—
	100	12.13	12.18	0.00740
	0	18.14	—	—
	120	17.41	17.31	0.00608
	160	17.02	17.03	0.00700
				mean: 0.00691
0.4655	0	10.02	—	—
	120	9.30	9.19	0.00600
	0	11.52	—	—
	150	10.45	10.49	0.00713
	0	13.19	—	—
	120	12.30	12.36	0.00742
	160	12.04	12.09	0.00719
	0	18.66	—	—
	120	17.78	17.83	0.00733
	160	17.65	17.56	0.00631
				mean: 0.00689

TABLE 1. (Continued.)

$C_{Na_2CO_3}$ normal.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.8405	0	10.51	—	—
	120	9.69	9.72	0.00683
	160	9.50	9.45	0.00631
	0	13.14	—	—
	120	12.46	12.35	0.00567
	0	14.30	—	—
	120	13.50	13.51	0.00667
	160	13.18	13.24	0.00700
	0	19.75	—	—
	120	18.87	18.96	0.00733
	160	18.73	18.69	0.00638
				mean: 0.00660
1.216	0	10.15	—	—
	120	9.40	9.45	0.00625
	160	9.15	9.21	0.00625
	0	13.40	—	—
	120	12.64	12.70	0.00633
	160	12.48	12.46	0.00575
	0	18.32	—	—
	120	17.68	17.62	0.00533
	160	17.49	17.38	0.00519
				mean: 0.00585

As is seen in Table 1, the oxidation velocity of stannous hydroxide is independent of the quantity of stannous hydroxide in sodium carbonate solution approximately, and the effect of the concentration of sodium carbonate on the oxidation velocity is small. The result shows that the oxidation of stannous hydroxide principally takes place in the liquid phase and not on the surface of the solid phase, as in the case of the oxidation of ferrous hydroxide suspended in sodium hydroxide solution by means of air.⁽¹⁾ We see also from the results that stannous hydroxide oxidizes very slowly in the air, and that the rapid increase of the oxidation velocity of stannous hydroxide with the increase of the concentration of sodium hydroxide⁽²⁾ is due to the formation of sodium stannite which is soluble in the solution.

The Effect of Temperature. The oxidation velocities observed at 30°C. and 40°C. are given in Table 2. The effect of temperature was very small.

(1) S. Miyamoto, this journal, 2 (1927), 40; *Scientific Papers of the Institute of Physical and Chemical Research*; 7 (1927), 35.

(2) S. Miyamoto, this journal, 2 (1927) 158; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 192.

TABLE 2.

Air = 7.78 litres per hour.

Temp.	C _{N₂O₃} normal.	<i>t</i> min.	<i>v</i> c.c.	<i>v</i> _{calc.} c.c.	<i>k</i>
30° C.	0.0155	0	10.26	—	—
		120	9.29	9.37	0.00808
		160	9.11	9.08	0.00719
		0	12.92	—	—
		120	12.09	12.03	0.00692
		160	11.95	11.74	0.00606
		0	19.32	—	—
		120	18.24	18.43	0.00900
		160	18.18	18.14	0.00713
					mean: 0.00740
30° C.	0.0905	0	10.12	—	—
		120	8.97	9.09	0.00958
		160	8.91	8.75	0.00756
		0	13.07	—	—
		120	12.09	12.04	0.00817
		160	11.87	11.70	0.00750
		0	18.88	—	—
		120	17.66	17.85	0.01017
		160	17.55	17.51	0.00831
					mean: 0.00855
40° C.	0.0155	0	9.75	—	—
		90	9.07	9.03	0.00756
		150	8.74	8.55	0.00673
		0	12.19	—	—
		90	11.49	11.47	0.00778
		160	11.05	10.91	0.00713
		0	17.84	—	—
		90	16.96	17.12	0.00978
		150	16.50	16.64	0.00893
					mean: 0.00799
40° C.	0.0905	0	9.81	—	—
		120	8.80	8.78	0.00842
		160	8.59	8.43	0.00763
		0	12.31	—	—
		120	11.27	11.28	0.00867
		160	11.15	10.93	0.00725
		0	18.39	—	—
		120	17.16	17.36	0.01025
		160	16.87	17.01	0.00950
					mean: 0.00862

$$\frac{k_{30^{\circ}}}{k_{20^{\circ}}} = \frac{0.00740}{0.00600} = 1.23 \quad \frac{k_{40^{\circ}}}{k_{30^{\circ}}} = \frac{0.00799}{0.00740} = 1.08, \text{ when } C_{Na_2CO_3} = 0.0155 \text{ normal}$$

$$\frac{k_{30^{\circ}}}{k_{20^{\circ}}} = \frac{0.00855}{0.00690} = 1.24 \quad \frac{k_{40^{\circ}}}{k_{30^{\circ}}} = \frac{0.00862}{0.00855} = 1.01, \text{ when } C_{Na_2CO_3} = 0.0905 \text{ normal}$$

The oxidation velocity of stannous hydroxide in sodium carbonate solution is thus very small and it was not studied thoroughly. More complete study will be carried out in later occasion.

Summary.

1. The oxidation velocity of stannous hydroxide suspended in sodium carbonate solution of various concentrations by means of air was studied. The oxidation velocity was independent of the quantity of stannous hydroxide.
2. The effect of the concentration of sodium carbonate on the reaction velocity was small.
3. It was ascertained that sodium stannite is oxidized rapidly, while stannous hydroxide is oxidized very slowly by means of air.
4. The effect of temperature on the reaction was small.

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ELECTRICAL CONDUCTANCE OF NICKEL SULPHATE SOLUTION AND IONIC CONDUCTANCE OF NICKEL.

By Kwanji MURATA.

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In the study of the electrode potential of nickel, the results of which will be presented in another paper by the writer, it was necessary to determine the degrees of ionization of its sulphate solutions.

The degree of ionization of a solution is usually expressed by the relation,

$$\alpha = \frac{\lambda}{\lambda_0} \left(\frac{\eta}{\eta_0} \right),$$

where λ is the equivalent conductance of the solution in question, λ_0 that of

an infinitely dilute solution of the electrolyte and η/η_0 is the relative viscosity of the solution which may be taken as unity for sufficiently dilute solutions.

Of these values, the equivalent conductances of nickel sulphate at various concentrations at 25° C. were determined separately by Franke and Jones.⁽¹⁾ However, as these values differ from each other in a not inconsiderable amount, conductivity measurements were made, taking full precaution in preparing the material and in the experiment. Viscosity measurements were also made in parallel.

The equivalent conductance at zero concentration can be calculated by Kohlrausch's principle of additivity from the ionic conductances of the nickel ion and the sulphate ion. Though there are several accurate determinations of the ionic conductance of the latter constituent, Heydweiller's value⁽²⁾ only is known for the ionic conductance of the former. He has derived this value from the values of equivalent conductance at zero concentration of nickel nitrate, chloride and bromide, which were obtained by the Kohlrausch method of plotting the equivalent conductances at various concentrations against the cube-root of the concentrations. But, his values of λ_0 thus obtained are not reliable, because of the too large extrapolation from the points at some high concentrations to that of the infinite dilution and it is therefore desirable to evaluate λ_0 by some other method of greater accuracy. For this purpose, however, the conductance values of nickel salts, given in Kohlrausch and Holborn's table, are not accurate enough and will lead to giving the value of the ionic conductance of nickel a probable error of more than a few percent.

Therefore, the value of λ_0 of nickel sulphate was obtained by Noyes' method⁽³⁾ of using Storch's function from the writer's own values of equivalent conductances at various concentrations, which were determined with sufficient accuracy.

Materials. *Conductivity Water.*—The conductivity water was prepared by the usual method of redistilling ordinary distilled water with alkaline permanganate and condensing it by means of a tin condenser. All the water used had a conductivity between 0.7×10^{-6} and 1.0×10^{-6} reciprocal ohm.

Nickel Sulphate Solutions.—Kahlbaum's cobalt-free nickel sulphate was purified by twice recrystallizations from conductivity water. The separate solutions of nickel sulphate were made up by diluting three standardized stock solutions, 1 N, 0.1 N, and 0.02 N, with the conductivity water to the

(1) Kohlrausch and Holborn, "Das Leitvermögen der Electrolyte."

(2) *Z. physik. Chem.*, **89** (1915), 281.

(3) Noyes and Falk, *J. Am. Chem. Soc.*, **34** (1912), 462.

accurate normality desired at 25° C. or 18° C.. The standardization of these stock solutions was made by an electroanalysis for nickel using a rotating anode.⁽¹⁾

Measurements of Specific Conductances. *Apparatus and Procedure.*—The conductivity was measured by the ordinary Kohlrausch bridge method, using two cells of the Washburn type A and B.⁽²⁾

The assembly for the measurement consisted of a Kohlrausch bridge with extension coils, a 5-dial Curtis-coil resistance box (both furnished by the Leeds and Northrup Company), Noguchi's special transformer producing a very audible alternating current suitable for the Kohlrausch bridge,⁽³⁾ and a tunable telephone. The slide-wire and the resistance box were calibrated just before the conductivity work was begun. The cell constants of the conductivity cells were first determined with a 1/10 normal solution of Kahlbaum's best potassium chloride, and were found to have the values of 1.6856 and 0.1754, respectively. Then these cell constants were checked by means of a 1/50 normal solution of potassium chloride.

The specific conductivities of the solutions were measured at $25^{\circ} \pm 0.02^{\circ} \text{C.}$ and at $18^{\circ} \pm 0.02^{\circ} \text{C.}$ Immediately after the preparation of each solution its conductivity was measured. After filling the conductivity cell, it was placed in the thermostat and left there for about half an hour. The conductance was then measured twice at an interval of fifteen minutes, in order to be assured that the solution had attained the temperature of the bath. Three separate readings with different resistances gave the conductances, which agree within 0.04 %. The cell was then emptied and refilled with the same solution and confirmative measurement was made. The various determinations of the conductance of the same solution using the same resistance agree within less than 0.02 %.

Results.—Table 1 contains the averages of the specific conductances thus obtained at 25° C. and the equivalent conductances calculated from them and Table 2, those at 18° C.

In both tables, the first column gives the concentration in equivalent per liter at the temperature of the measurement; the second, the cell constant; the third, the measured specific conductance in reciprocal ohms, after the correction for instrumental errors (in the slide wire and the resistance coils); and the fourth, the true specific conductance after the water correction, obtained by subtracting the conductance of water from the value of observed specific conductance in the third column. The mean value of the specific conductances of water was 1.02×10^{-6} at 25° C. and

(1) Treadwell-Hall, "Analytical Chemistry" II, p. 136.

(2) *J. Am. Chem. Soc.*, **38** (1916), 2449.

(3) *J. of Inst. of Electrical Engineers of Japan*, (1921) 394; (1923), 421.

0.81×10^{-6} at 18°C . in reciprocal ohm. The last column gives the equivalent conductance calculated from the value of the corrected specific conductance in the fourth column.

TABLE 1.
Conductance of Aqueous Nickel Sulphate Solution at 25°C .

Concentration at 25°C .	Cell constant.	Specific conductance.		Equivalent conductance.
		Observed.	Corrected.	
1	1.6856	29091 $\times 10^{-6}$	29091 $\times 10^{-6}$	29.091
0.5	"	17611 "	17611 "	35.222
0.2	"	8717 "	8717 "	43.585
0.1	"	5075.5 "	5075.5 "	50.755
0.05	"	2958.0 "	2958.0 "	59.160
0.02	0.1754	1446.1 "	1445.1 "	72.254
0.01	"	827.9 "	826.9 "	82.69
0.005	"	466.82 "	465.8 "	93.16
0.002	"	212.00 "	210.98 "	105.49
0.001	"	114.07 "	113.05 "	113.05
0.0005	"	60.35 "	59.331 "	118.66
0.0002	"	25.85 "	24.827 "	124.14
0.0001	"	13.71 "	12.690 "	126.90

TABLE 2.
Conductance of Aqueous Nickel Sulphate Solution at 18°C .

Concentration at 18°C .	Cell constant.	Specific conductance.		Equivalent conductance.
		Observed.	Corrected.	
1	1.6856	25066 $\times 10^{-6}$	25066 $\times 10^{-6}$	25.066
0.5	"	15185 "	15185 "	30.370
0.2	"	7519 "	7519 "	37.595
0.1	"	4383.3 "	4383.3 "	43.833
0.05	"	2550.4 "	2550.4 "	51.008
0.02	0.1754	1241.2 "	1240.4 "	62.02
0.01	"	709.7 "	708.9 "	70.89
0.005	"	398.2 "	397.4 "	79.48
0.002	"	180.68 "	179.87 "	89.94
0.001	"	97.12 "	96.31 "	96.31
0.0005	"	51.31 "	50.50 "	101.00
0.0002	"	21.884 "	21.074 "	105.37
0.0001	"	11.680 "	10.870 "	108.70

Calculation of Equivalent Conductance of Nickel Sulphate at Infinite Dilution and Ionic Conductance of Nickel. The value of λ_0 of nickel sulphate was obtained by employing the graphic method of A.A. Noyes.⁽¹⁾

The method is as follows: Storch's function $C(\lambda_0 - \lambda) = k(C\lambda)^n$, which is equivalent to $\frac{C\alpha}{C(1-\alpha)} = k$, if $\frac{\lambda}{\lambda_0}$ may be taken as a measure of the ionization (α), is transformed into $\frac{1}{\lambda_0} = \frac{1}{\lambda} - k(C\lambda)^{n-1}$, and the values of $(C\lambda)^{n-1}$ in the range from 0.0001 to 0.02 normal are plotted as abscissas against the values of $\frac{1}{\lambda}$ as ordinates, by varying the values of $(n-1)$, until a plot as linear as possible is obtained. The value of λ_0 is obtained graphically by the extrapolation of the plotted line to zero concentration or $C\lambda = 0$. In Fig. 1, in order to make the various curves comparable, the value $(C\lambda)^{n-1}$ for the highest concentration (0.02 normal) was made 100 for each value of n and the other values were proportionally varied by multiplying by the appropriate factors.

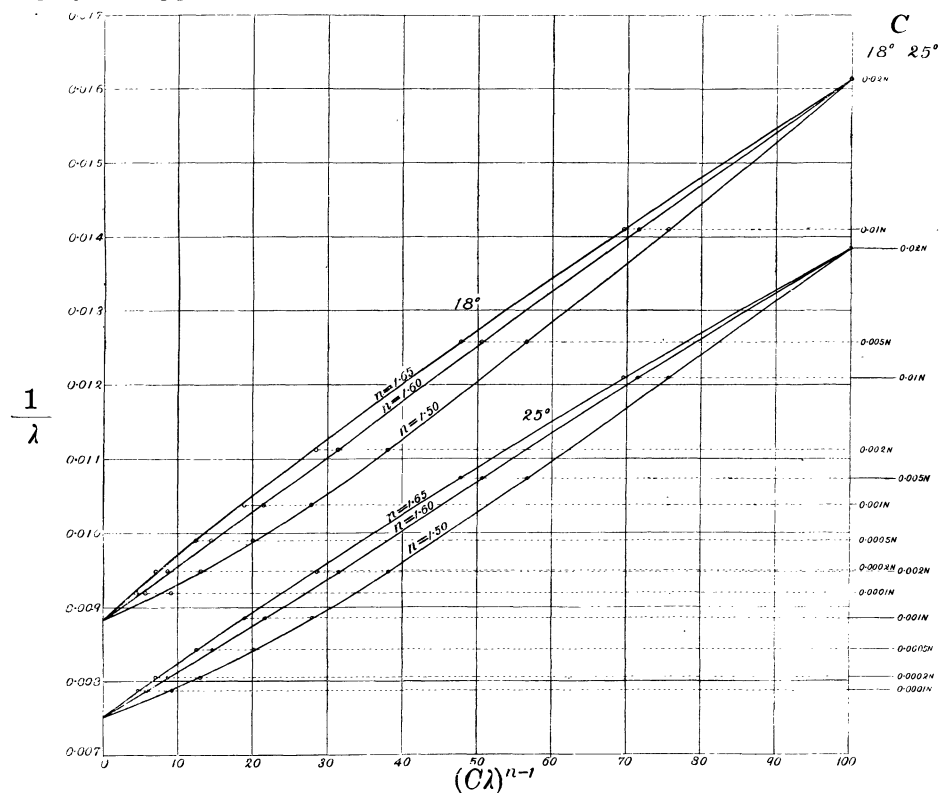


Fig. 1.

(1) Noyes and Johnston, *J. Am. Chem. Soc.*, **31** (1909), 987; Noyes and Falk, *ibid.* **34** (1912), 454.

It will be seen from Fig. 1, that the values of the exponent at 25° C. and 18° C. for nickel sulphate were found to be 1.6 in each case for the concentration interval from 0.0001 to 0.02 normal.

It has been found by Noyes and his co-workers that lines nearly straight were obtained with almost the same values of n for the salts of similar type, and according to Noyes and Falk (loc. cit.) for all bi-bivalent sulphates n takes a value not far from 1.6 for the concentration interval from 0.0001 to 0.02 normal. Noyes also pointed out that the variation of the exponent with the temperature is insignificant. Similar results were obtained in the case of nickel sulphate.

Table 3 contains the λ_0 values and the ionic conductances of nickel ion ($\lambda_{\frac{1}{2}Ni}$) computed therefrom and Heydweiller's values are also inserted for comparison.

TABLE 3.

Temperature.	Author.			(Heydweiller.) $\lambda_{\frac{1}{2}Ni^{++}}$
	λ_0	$\lambda_{\frac{1}{2}Ni^{++}}$		
		(I)	(II)	
18° C.	113.6	45.1	45.6	44.
25° C.	133.0	53.0	54.2	52.1

As the value of the ionic conductance of nickel changes in accordance with the value that is taken for the ionic conductance of the sulphate ion, in the calculation of the value in column (I), the necessary datum of $\lambda_{\frac{1}{2}SO_4}$ was obtained from Noyes and Falk's table (loc. cit.) and for column (II), the value of $\lambda_{\frac{1}{2}SO_4}$ in Kohlrausch-Holborn's table was used.

The Relative Viscosity and Degree of Ionization of 1/20 M. Nickel Sulphate. The measurements of relative viscosity were made with Ostwald's viscosimeter and the relative viscosity of 0.05 molal nickel sulphate at 18° C., and 25° C. was found to be 1.0209 and 1.0175, respectively.

The degrees of ionization at this concentration are obtained by using the above corresponding values of λ , λ_0 and η/η_0 at each temperature, thus :

$$\alpha \text{ at } 18^\circ \text{ C.} = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{43.833 \times 1.0209}{113.6} = 0.3883$$

$$\alpha \text{ at } 25^\circ \text{ C.} = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{50.75 \times 1.0175}{133.0} = 0.3939$$

Summary.

1. The conductances of aqueous solutions of nickel sulphate at concentrations 0.0001 to 1 equivalent per liter at 25° C. and 18° C. were measured and the equivalent conductances at infinite dilution were found.

2. The ionic conductances of nickel also were calculated.

3. The relative viscosity and the degree of ionization of 1/20 mol nickel sulphate were calculated.

In conclusion, the writer wishes to express his thanks to Professor G. Fuseya for his kind direction.

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THE CONSTITUENTS OF *TYPHA ANGUSTATA*,
BORY. ET CHAUB.

By Masao FUKUDA.

Received December 20, 1927. Published February 28, 1928.

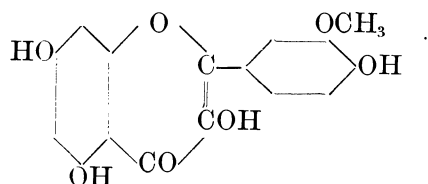
The plant, *Typha angustata*, Bory. et Chaub., belongs to the *Typhaceae*. Its pollen has been used medicinally from remote antiquity in the East as a diuretic and a styptic. So far as I am aware, no chemical examination of this pollen appears to have been made. For the purpose of investigating its chemical constituents, it was first extracted with hot alcohol. After evaporating most of the alcohol, the residue was separated into two parts by treatment with petroleum ether.

From the soluble part in petroleum ether, a colourless substance, m.p. 62.5–63°, was obtained. The composition of this substance was $C_{16}H_{32}O_2$, and its constitution was found to be palmitic acid by analysis, molecular weight determination, and by the method of mixed melting point.

The insoluble part in petroleum ether gave a characteristic reaction to flavone by treatment with metallic magnesium and hydrochloric acid and, after being hydrolysed with sulphuric acid and then neutralised with sodium hydroxide, it reduced Fehling's solution. From these facts, this part appears to contain a glucoside of flavone. With the view to isolate the glucoside, the part was extracted with hot water, the solution precipitated with lead acetate, and the filtrate treated with basic lead acetate, by which

means a second lead precipitate was formed. The latter was decomposed with acetic acid and, after being freed from the soluble lead salt with sulphuric acid, the excess of the sulphuric acid was neutralised with barium carbonate and the barium sulphate thus precipitated was then filtered. Since the glucoside could not be obtained in a crystalline state after these treatments, it was then hydrolysed with dilute sulphuric acid, when a yellow substance (A) separated, which was collected and washed with water. From the filtrate, *d*-phenylglucosazone, m.p. 203–204°, was obtained by treatment with phenylhydrazine and acetic acid, and *p*-bromobenzoylhydrazone was also formed by the action of *p*-bromobenzoylhydrazine on it, which is soluble in a boiling mixture of alcohol, chloroform and water. These facts point to the presence of *d*-glucose in the filtrate.

The yellow substance (A) had a composition, $C_{16}H_{12}O_7$, and melted at 307°. The presence of four hydroxyl groups in the compound was proved by the formation of the tetra-acetyl derivative, $C_{16}H_8O_7(C_2H_3O)_4$, m.p. 205° and the existence of one methoxyl group, by the micro-Zeisel method. The compound, on decomposition with sodium hydroxide, gave phloroglucinol as a phenolic decomposition product and vanillic acid, as an acidic one. From these results, the constitution of substance (A) appears to be *isorhamnetin* :



Since there was no authentic specimen of *isorhamnetin*, the author confirmed the identity of substance (A) with it by synthesising the latter by Robinson's method,⁽¹⁾ and comparing their acetyl derivatives.

Experimental.

About 20 kilos. of the material were extracted by boiling with 70 % alcohol for six hours in the portion of 250 grams, 1250 c.c. of the alcohol being used for each 250 grams of the material. After the removal of most of the alcohol, the remaining alcoholic solution was shaken with petroleum ether, b.p. 50–80°, and the petroleum ether solution (a) and the alcoholic residue (b) were treated as follows :

A portion of the petroleum ether solution (a) was then mixed with acetone, when colourless crystals were deposited, which, after being recryst-

(1) *J. Chem. Soc.*, 1926, 2336.

tallised from methyl alcohol, melted at 60.5–61.5°. The filtrate was evaporated and the residual oil was distilled under a reduced pressure of 2–3 mm., when the distillate melted at 61–61.5° after recrystallisation from methyl alcohol and produced no depression of the melting point by admixture with the above specimen. After this preliminary experiment, the main portion of the petroleum ether solution (a) was evaporated and the residual oil was distilled under a diminished pressure of 2–3 mm. After recrystallising it four times from methyl alcohol, colourless crystals melting at 62.5–63° were obtained (Found: C = 74.80; H = 12.71; Mol. wt., by Rast's method, 248; 254. $C_{16}H_{32}O_2$ requires C = 74.92; H = 12.59 %. Mol. wt., 256. 3).

Titration: 0.5000 gr., dissolved in alcohol, neutralised 21.04 c.c. of an 0.0926-*N* solution of alcoholic potash, whereas this amount of a monobasic acid, $C_{16}H_{32}O_2$, should neutralise 21.07 c.c.

The identity of this acid with palmitic acid was proved by the fact that the mixture of the acid with an authentic specimen of palmitic acid caused no depression of the melting point.

After being combined with the alcoholic residue (b) from several separate experiments, it was further concentrated to 4 litres under diminished pressure, diluted with 24 litres of water and heated on a water-bath for 2.5 to 3 hours. The light, brown, aqueous solution thus obtained was again evaporated to one-fourth of its bulk.

(1) **The Determination of Reducing Sugar combined with Flavone.** The glucoside of flavone was precipitated by basic lead acetate, the precipitate was decomposed with dilute acetic acid (50 %) and freed from the soluble lead compound with sulphuric acid. The excess of sulphuric acid was then neutralised with barium carbonate, and the barium sulphate thus precipitated was filtered. As the glucoside of flavone was difficult to obtain in a crystalline state, sulphuric acid was added till the solution contained 4 per cent of this acid and heated on a water-bath, when a yellow substance (A) was obtained, which was collected and washed well with water. The yield was 50 grams. A portion of the filtrate was warmed with phenylhydrazine and glacial acetic acid, when brownish yellow crystals separated. After being recrystallised from alcohol, the crystals melted at 203–204° and caused no depression of the melting point by admixture with *d*-phenylglucosazone. In order to decide whether the reducing sugar is glucose or mannose, another portion of the filtrate was treated with acetic acid and *p*-bromobenzoylhydrazine, when colourless crystals were obtained, which were clearly dissolved in a boiling mixture of alcohol, water and chloroform. It thus follows that the reducing sugar is *d*-glucose.

(2) **The Determination of Yellow Substance (A).** After being recrystallised from methyl alcohol, it separated in lemon-yellow crystals, m.p. 307° (decomp.) (Found: C = 60.61; H = 3.99; CH_3O , by the micro-Zeisel method = 9.58; Mol. wt., by the Rast method, 303. $\text{C}_{16}\text{H}_{12}\text{O}_7$ requires C = 60.74; H = 3.80; CH_3O = 9.80 %. Mol. wt., 316).

The Acetyl Derivative. This compound was prepared by heating the substance with acetic anhydride and fused sodium acetate, and melted at $204\text{--}205^{\circ}$ (Found: C = 59.59; H = 4.28. $\text{C}_{24}\text{H}_{20}\text{O}_{11}$ requires C = 59.51; H = 4.13 %).

The Decomposition of Yellow Substance (A) with Sodium Hydroxide. The substance (1 gram) was dissolved in a solution of 2 grams of sodium hydroxide in 12 c.c. of water and a current of air was passed through it for three hours, when the colour of the solution turned a brownish yellow. The solution was neutralised with sulphuric acid, and, after an excess of sodium bicarbonate had been added, it was extracted with ether. The ethereal solution (c) and the aqueous residue (d) were treated in the following way:

(c) After the removal of the ether, the residue was recrystallised from water with the addition of animal charcoal, when colourless crystals were obtained, which, drying at $105\text{--}110^{\circ}$, melted at $216\text{--}217^{\circ}$. This substance did not depress the melting point after being mixed with anhydrous phloroglucinol, being undoubtedly identical with the latter.

(d) The aqueous residue was acidified with hydrochloric acid and extracted with ether. After evaporating the ether from the ethereal solution, the residue was recrystallised from water with the addition of animal charcoal. The substance thus purified melted at $206\text{--}207^{\circ}$ and its melting point was not depressed by admixture with an authentic specimen of vanillic acid.

Synthesis of isoRhamnetin. In order to prove the identity of yellow substance (A) with *isorhamnetin*, the latter was synthesised by Robinson's method.

For this purpose, vanillic acid was first synthesised by a modification of the method described in the report on the German patent No. 258887. *isoRhamnetin* was then synthesised from vanillic acid by following exactly the directions given by Robinson and converted into the tetra-acetyl derivative, m.p. $204\text{--}205.5^{\circ}$. The melting point of this substance was not depressed by admixture with the acetyl derivative of yellow substance (A), thus leaving no doubt as to identity of yellow substance (A) with *isorhamnetin*.

In conclusion, the author wishes to express his sincere thanks to Professor Hideo Maniwa, Chiba Medical College, by whose suggestion this investigation was made, and to Professor Hiroshi Nomura for his kind guidance during the investigation.

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ELECTRODE POTENTIAL OF NICKEL.

PART I. MEASUREMENTS IN AN ATMOSPHERE OF HYDROGEN WITH REDUCED NICKEL POWDER.

By Kwanji MURATA.

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Although much has been written concerning the phenomena which are observed when nickel is involved in the electrolytic process, only a small amount of work has been published dealing with the direct determination of the electrode potential of nickel, and as the measured values of the electrode potential, as shown in Table 1, can by no means be said to be in agreement with one another, it is desirable to find some means of making a reliable nickel electrode which will give a reproducible, constant, and reversible potential.

TABLE 1.
The equilibrium potential of nickel in N/1 NiSO₄ solution.

B. Neumann, <i>Z. physik. Chem.</i> , 14 (1894), 215.	-0.255 volt
A. Siemens, <i>Z. anorg. Chem.</i> , 41 (1904), 249.	-0.221 „
H. Euler, <i>Z. anorg. Chem.</i> , 41 (1904), 93.	-0.183 „
W. Muthmann & F. Fraunberger, <i>Sitz. Bayer. Akad. Wiss.</i> , 34 (1904), 201.	-0.597 „
E. P. Schoch, <i>Amer. Chem. Journ.</i> , 41 (1909), 208.	-0.197 „
A. Schweitzer, <i>Z. Elektrochem.</i> , 15 (1909), 607.	-0.33 „
R. Schildbach, <i>Z. Elektrochem.</i> , 16 (1910), 967.	-0.25 „
A. Smits and Lobry de Bruyn, <i>Proc. Acad. Sci. Amsterdam</i> , 20 (1918), 394.	-0.197 „
The writer (calculated* from the normal electrode potential)	-0.276 „

* The other necessary data for this calculation were obtained from the writer's paper on the conductance of nickel sulphate solution (this journal, **3** (1928), 47). The value of relative viscosity was obtained by assuming that its deviation from unit is approximately proportional to the concentration.

A close study of previous works on the nickel electrode potential, above cited, especially those by Schoch, Schildbach and Schweitzer and the works of Richards and Behr⁽¹⁾, Foerster⁽²⁾ and Schildbach on the electrode potentials of the metals of the same group, i.e. iron and cobalt, show why the observed values of the electrode potential of nickel differ one from another.

(1) Richards and Behr, *Z. physik. Chem.*, **58** (1907), 301.

(2) Foerster, *Abhandl. Deut. Bunsen Gesellsch.*, No. 2 (1909).

The potential of nickel electrode changes very considerably with the mode of preparation, previous treatment, and the state of the electrode, which causes can be divided into two factors, i.e. physical and chemical. Schoch and Schweitzer obtained higher and more constant values of the electrode potential with powdered nickel than with solid. It is well known that this physical factor has a similar effect on the electrode potential in the cases of other metals also and that the finely divided state of the metal is more favourable for the reproducibility and the constancy of the electrode. It has been suggested by G. N. Lewis⁽¹⁾ that the lack of reproducibility in the case of solid metal is due to the highly strained condition or unstable physical state of the metal whether it be produced by rolling or by electrolysis. Then it is natural that there is no agreement even in the measurements of these two investigators both working with powder but from different sources. Turning to the chemical factor, it is an important fact, observed definitely by Schoch, that the potential is diminished by the presence of air and increased by the introduction of hydrogen into the cell. As this effect of oxygen is rather specific to metals of the iron group and to chromium, it must have a close relation with the phenomena of passivity. It is therefore necessary to avoid any contact with oxygen by both the electrode and the solution, for the purpose of obtaining the true potential of active nickel. In this respect the above three investigators were careful in preparing the electrolyte and they boiled the solution before introducing it into the cell. On the other hand, in their mode of preparation of the electrode there still remains a little which leads us to suspect that they did not measure the true potential of active nickel. All the nickel used were those which had been kept in air and even the reduced nickel powder used by Schoch must have had the probable chance of coming into contact with the air while moving from the furnace into the cell. Schweitzer in all of his experiments polarised the electrodes cathodically in the cell with a solution of caustic potash to reduce any trace of oxide on the surface and, after washing, filled the cell with the electrolyte entirely in the absence of air. Schoch also once used the polarised electrode. As for the results with such electrodes, full discussion will be made later together with the results of the writer's experiments with polarised electrodes.

The writer obtained a reproducible and fairly constant electrode which gave a reversible electrode potential of active nickel by using powder electrode reduced in the cell, and using an apparatus which allows the cell to be filled in an atmosphere of hydrogen. But, as Schoch, and Richards and Behr reported that the occluded hydrogen raises the potential of nickel

(1) Lewis and Randall, "Thermodynamics," (1923), p. 388.

or iron, similar experiments were made in an atmosphere of nitrogen and in an atmosphere of a mixture of nitrogen and hydrogen, the results of which experiments might lead to the conclusion that the occluded hydrogen has no effect in the case of nickel. The report on those latter experiments will be made in the second part of this paper which will be published in the very near future.

Materials. *Water.*—Throughout the experiment conductivity water which had a specific conductance of less than 1.2×10^{-6} was used.

Nickel Oxide.—The nickel oxide was prepared by precipitation from a hot (90°C.) dilute (1%) solution of Kahlbaum's cobalt-free nickel nitrate with redistilled ammonia, washed thoroughly by decantation and filtration and dried. The dried material was crushed in an agate mortar into powder and then heated, to remove any nitrate that remained, in a furnace by passing an air current for about six hours at 600° to 700°C. and for one additional hour at 700° to 800°C.

Electrolyte.—In the experiments, nickel sulphate was employed as the electrolyte, because uni-bivalent salt is liable to form intermediate ions, and also for the convenience of comparing the result of these measurements with those of the previous investigators. Kahlbaum's cobalt-free sulphate was recrystallized twice from conductivity water and used. The concentrations were determined by electrolysis for nickel⁽¹⁾.

Apparatus and General Procedure. As was stated above the half cell for the nickel electrode was so designed as to allow the reducing of powdered

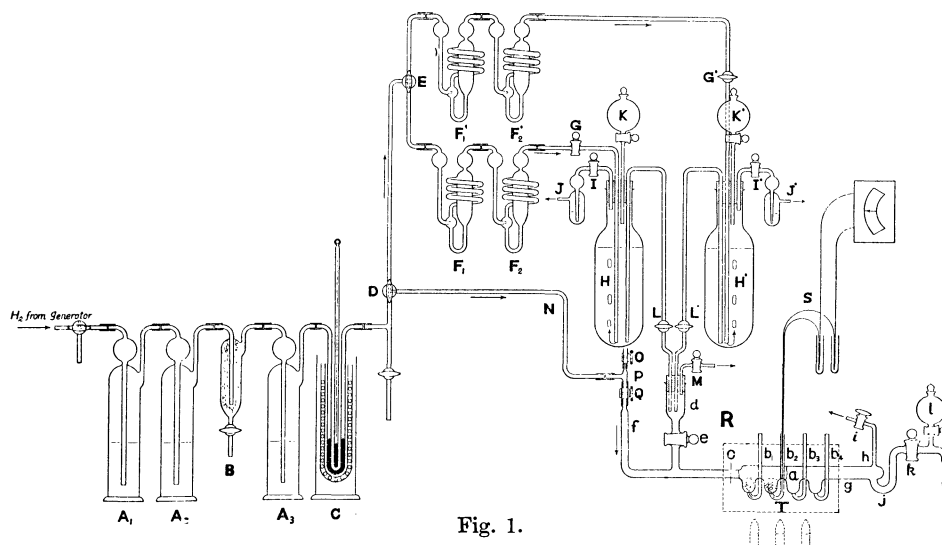


Fig. 1.

(1) Treadwell-Hall, "Analytical Chemistry" II, (1915), p. 136.

nickel oxide with hydrogen directly in the cell, and if desired, of permitting prolonged evacuation at high temperature to remove hydrogen occluded in the nickel electrode. And the apparatus was so arranged that the electrolyte could be transferred into the cell without contact with air.

Fig. 1 shows the whole arrangement of the apparatus and the half cell. R is the electrode vessel which is made of glass, having four separate electrode compartments b_1, b_2, b_3, b_4 . At the bottom of each compartment a platinum wire was sealed and was covered with finely powdered nickel oxide. The cell is provided with two sealed-on inlet tubes, one tube, f, which serves for hydrogen and the other, d, for the solution.

To introduce the nickel oxide into the vessel, the inlet side was cut off from the compartment part, a, at a point, marked c in the figure, as close as possible to the compartments, so that any nickel oxide which may adhere to the inner wall of the tube, c, may be reduced at the same temperature zone of the oven as is the oxide in the electrode compartments. After the introduction of nickel oxide the two parts were joined together and then the electrode vessel was connected with the other parts of the apparatus as shown in the figure.

The oven, T, was made of copper plate covered with thick asbestos plates and packed with asbestos fiber.

The hard glass flask H, of the capacity of 250 c.c. was the reservoir of a nickel sulphate solution and was fitted with a rubber stopper covered with bees-wax. Through this stopper was fitted a separating funnel K which served for conducting the solution into the flask and three tubes; one is an inlet of hydrogen, one which is connected to the trap J containing the same solution is an outlet of hydrogen, and the other one serves for introducing the solution into the electrode vessel. The other end of the tube L was thrust through the rubber stopper into one of the inlet tubes of the electrode vessel, d. Another flask, H', of the same construction, served for the solution of the other concentration.

The hydrogen used was generated from Kipp's apparatus by the action of hydrochloric acid on Kahlbaum's C.P. zinc or pure electrolytic zinc and was purified by successively passing it through three alkaline solutions of potassium permanganate A_1, A_2, A_3 , a layer of glass wool, B, and then over heated, fresh, palladized asbestos in the tube, C, to remove any trace of oxygen that might be present. Then the gas could be saturated with water vapour, before entering into the flask H, or H' by passing humidifiers F_1 and F_2 , or F_1' and F_2' with the same solution as is contained in the flask. Before the operation was started, all the parts of the apparatus were tested for its air-tightness.

In the reduction of nickel oxide, the hydrogen was introduced into the cell through the tube N, until all the air in the electrode vessel was washed out, with cocks i, k and then e, M being open.

The oven was put in its place and was gradually heated with three Bunsen burners. It was noticed that the reduction usually began at about 200°C., as was evidenced by the appearance of condensed water in the outlet tube of the gas. But the most part of the reduction was performed at 300°C. which is a temperature below the recognized transition point of nickel and the furnace was kept at this temperature for one hour more after the ceasing of water evolution, for the purpose of the assurance of complete reduction. During this operation the flow of hydrogen was kept at a rate of two or three bubbles per second. The condensed water was allowed to fall in the bent tube j, and to flow out from time to time through k by the pressure of hydrogen. Then the cell was left to cool to the room temperature, and was ready for being filled with the electrolyte, having been removed the furnace.

On the other hand, the electrolyte was freed from air in the following manner. Approximately the required amount of nickel sulphate solution was placed in the flask and purified hydrogen from the humidifiers was introduced into the flask. The gas bubbling up in small bubbles, saturating and stirring the whole liquid, left the flask through a trap. At the same time a part of the hydrogen was introduced into this reservoir also through the path N, e, L to replace the air in the tube L with hydrogen. After most of the air in the flask had been replaced by hydrogen, the stopcock G was closed and the flask was evacuated by an oil pump attached to the trap J. A mercury trap was also connected between the flask and the pump to prevent any back flow of air. G was then opened and the gas was readmitted slowly. This operation was repeated several times and the solution was made as free as possible from air and then the solution was preserved in the flask under an atmosphere of hydrogen to prevent the diffusion of oxygen from the atmosphere.

The electrolyte was allowed to flow down into the cell by the pressure of the gas. With the form of construction shown, it is an easy matter to fill the cell without leaving any bubbles of gas. The reservoir, l, of the cell was also filled with the same solution which served to rinse out the tube. The half-cell was then disconnected and placed in the thermostat where it was allowed to stand for half an hour before the electromotive force measurements were made. The filling up of the cell usually took about half an hour and therefore the first measurement was made one hour after the instant of the contact of the electrolyte with the nickel electrode. All the electromotive force measurements were made in a water thermostat, which was kept constant within 0.02°C.

For the measurements a Leeds and Northrup's K-type potentiometer and an H-type mirror galvanometer were used. As a standard of potential difference a Weston standard cell, which had been standardized by the Electrotechnical Laboratory of the Department of Communications, was used. A U-tube was used as the vessel for the junction solution. The decinormal calomel electrodes used were made from calomel prepared electrolytically and Kahlbaum's C.P. potassium chloride, and their potentials agreed very well with one another.

Results of Measurements of E.M.F. The combination of the cell was as follows :

$\text{Ni} \mid \text{NiSO}_4 (0.05 \text{ or } 0.005 \text{ M}) \mid \text{saturated KCl} \mid \text{KCl} (0.1 \text{ N}), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}.$

Table 2 contains the results of a series of measurements made on the cells of the solutions of the two different concentrations i.e. 0.05 M and 0.005 M. The time elapsed gives the hours after the contact of the electrolyte with the electrode.

TABLE 2.

E.M.F. of cell : $\text{Ni} \mid \text{NiSO}_4 \mid \text{sat. KCl} \mid \text{KCl}(0.1\text{N}), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$, at $25^\circ\text{C}.$

Elapsed time in hours	E.M.F. in volt.			
	0.05 M $\text{NiSO}_4/\text{L}.$		0.005 M $\text{NiSO}_4/\text{L}.$	
	Cell No. 1.	Cell No. 2.	Cell No. 3.	Cell No. 4.
1	-0.63860*	-0.63840	-0.66095*	-0.66032
2	-0.63860*	—	-0.66093*	-0.66030
3	—	—	—	-0.66255
4	-0.63858*	—	-0.66085*	—
12	-0.63846*	—	—	—
15	—	—	—	-0.6600
20	—	—	—	-0.6598
22	-0.63832**	—	-0.6604**	—
24	-0.63830**	—	—	—
36	-0.63810**	—	—	—
48	-0.63790**	—	-0.6600**	—
	H_2 on			
50	-0.63790	—	—	—
60	-0.63785	—	—	—

* After these measurements with cells Nos. 1 and 3 the temperature of the thermostat was lowered to $18^\circ\text{C}.$ and measurements were made at this temperature, the results of which are given in Table 3.

** After the measurements at $18^\circ\text{C}.$, the temperature was again raised to $25^\circ\text{C}.$ and these measurements were made.

Each two of the platinum electrode wires of each cell were coated electrolytically with nickel from ammoniacal nickel sulphate solution, and covered with nickel powder in the manner already stated. The electrode thus prepared, having been annealed at about 300°C. gave the potential which agrees with that of the naked platinum, covered with nickel powder within about 0.05 millivolt.

The agreement of the potential of each two cells with the solution of the same concentration and constancy is very good as compared with the results of the previous investigators. The change in potential of the same cell was not greater than 0.5 millivolt for 24 hours. Furthermore, the electromotive force was reversible with respect to temperature as will be shown in the next paragraph. Besides, it was observed that the electromotive force changed by not more than 0.05 millivolt by the passage of hydrogen through the solution in the cell for about half an hour which was done at the end of the measurements with cell No. 1 and also that by shaking the powdered electrode, the values of the electromotive forces fluctuated around a certain corresponding value temporarily, but did not show any tendency to change continuously in one direction.

The measurements of the electromotive force were made also at 18°C. with cells Nos. 1 and 3, after twelve hours measurement at 25°C. in the case of the former cell and after four hours measurement in the case of the latter. The results at 18°C. are given in Table 3.

After the measurements at 18°C., the temperature was again raised to 25°C. and further measurements were made, the results of which are given in Table 2. It will be observed that there is no hysteresis but only a continuous and slow lowering of the electromotive force.

TABLE 3.

E.M.F. of cell : $\text{Ni} | \text{NiSO}_4 | \text{sat. KCl} | \text{KCl}(0.1 \text{ N}), \text{Hg}_2\text{Cl}_2 | \text{Hg}$, at 18°C.

	Mols NiSO_4 per litre	E.M.F. in volt.
Cell No. 1	0.05	-0.63820
Cell No. 3	0.005	-0.66105

By the combinations of data for cells No. 1 and No. 3, given in Table 2 and Table 3, it will be found that the difference in electromotive force between 18°C. and 25°C. are 0.00066 and 0.00020 volt for the cells of 0.05 and 0.005 mol, respectively. Taking the difference in the potential of the standard decinormal calomel electrode between these two temperatures as

−0.00040 volt⁽¹⁾, the temperature coefficients of these cells are calculated to be :

$$\frac{\Delta E}{\Delta t} = -0.00009 \text{ volt per degree for the } 0.05 \text{ mol NiSO}_4.$$

$$\text{''} = -0.00003 \text{ '' '' '' '' '' } 0.005 \text{ '' '' }.$$

Calculation of Normal Electrode Potential. The normal electrode potential was computed on the ground of two different concepts of the strong electrolytes, one being that the ion concentration is involved in the expression of the electromotive force of the concentration cell and the other being that the activity of the ion is involved.

(1) *Ion concentration being used.* The normal electrode potential E_0 can be calculated by using the following well-known equation

$$E = E_0 + \frac{RT}{2F} \ln Ca \quad (1)$$

where E is the potential in the solution used, referred to the molal hydrogen electrode, C is the concentration of the solution in mols per litre and α is its degree of ionization which is defined by $\frac{\lambda}{\lambda_0}$ for a dilute solution or by $\frac{\lambda\gamma}{\lambda_0\gamma_0}$ for a concentrated solution. As the values of λ , and ionic conductance of nickel ion, from which λ_0 must be calculated, given in Kohlrausch-Holborn's table of conductances are inaccurate and the viscosity data are lacking, the writer's own values were used⁽²⁾.

The data in Table 2 give, as a mean value for the cell,

Ni | NiSO₄(0.05 M) || KCl(0.1 N), Hg₂Cl₂ | Hg; $e = -0.6385$ volt at 25°C.

Taking the potential of the decinormal calomel electrode, E_c , to be −0.3376 volt, H₂ | H⁺(1 M) || KCl(0.1 N), Hg₂Cl₂ | Hg; $E_c = -0.3376$ volt, then Ni | NiSO₄(0.05 M) || H⁺(1 M) | H₂; $E = -0.3009$ volt.

For 0.05 M nickel sulphate solution, the values of λ , λ_0 and $\frac{\gamma}{\gamma_0}$ at 25°C. are 50.75, 133.0 and 1.0175, respectively and

$$\alpha = \frac{\lambda\gamma}{\lambda_0\gamma_0} = \frac{50.75 \times 1.0175}{133.0} = 0.3883$$

Then, we obtain $-0.3009 = E_0 + 0.02958 \log 0.05 \times 0.3883$
from which $E_0 = -0.2503$ volt at 25°C.

Similarly, as the mean value for the cell,

Ni | NiSO₄(0.005 M) || KCl(0.1 N), Hg₂Cl₂ | Hg; $e = -0.6607$ volt at 25°C.

and H₂ | H⁺(1 M) || KCl(0.1 N), Hg₂Cl₂ | Hg; $E_c = -0.3376$ volt at 25°C.

Combining these two, we obtain

$$\text{Ni} | \text{NiSO}_4(0.005 \text{ M}) || \text{H}^+(1 \text{ M}) | \text{H}_2; \quad E = -0.3231 \text{ volt at } 25^\circ\text{C}.$$

(1) Clark, "Determination of hydrogen ions," (1920), p. 203.

(2) This journal, 3 (1928), 47.

Taking $\frac{\lambda}{\lambda_0} = 82.69/133 = 0.62173$ as the degree of ionization of 0.005 M NiSO_4 . By equation (1), we obtain

$$-0.3231 = E_0 + 0.02958 \log 0.005 \times 0.62173$$

from which

$$E_0 = -0.2489 \text{ volt at } 25^\circ\text{C.}$$

Consequently, as a mean value of the potential for the electrode $\text{Ni} | \text{Ni}^{++}(1\text{M})$, we find

$$E_0 = -0.2496 \pm 0.0007 \text{ volt at } 25^\circ\text{C.}$$

In a similar manner, E_0 at 18°C. was calculated. The electromotive force of the cell,



Taking the potential of the decinormal calomel electrode to be -0.3380 volt, then,

$$\text{Ni} | \text{NiSO}_4(0.05 \text{ M}) || \text{H}^+(1 \text{ M}) | \text{H}_2; \quad E = -0.3002 \text{ volt.}$$

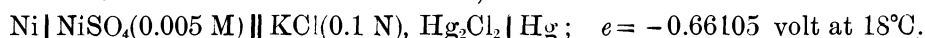
For 0.05 M NiSO_4 , the values of λ , λ_0 and $\frac{\gamma}{\gamma_0}$ at 18°C. are 43.833, 113.6 and 1.0209, respectively and

$$\alpha = \frac{\lambda\gamma}{\lambda_0\gamma_0} = \frac{43.833 \times 1.0209}{113.6} = 0.3939.$$

Inserting these values in equation (1), we obtain

$$\begin{aligned} -0.3002 &= E_0 + 0.02888 \log 0.05 \times 0.3939 \\ E_0 &= -0.2509 \text{ volt at } 18^\circ\text{C.} \end{aligned}$$

The electromotive force for the cell,



Subtracting the potential of the decinormal calomel electrode from this value, we obtain $\text{Ni} | \text{NiSO}_4(0.005 \text{ M}) || \text{H}^+(1 \text{ M}) | \text{H}_2; \quad E = -0.32305 \text{ volt.}$

And,

$$\alpha = \frac{\lambda}{\lambda_0} = \frac{70.89}{113.6} = 0.62403.$$

Then,

$$E_0 = -0.2507 \text{ volt at } 18^\circ\text{C.}$$

We find, as a mean value,

$$E_0 = -0.2508 \pm 0.0001 \text{ volt at } 18^\circ\text{C.}$$

(2) *Activity of the ion being used.* If the activity of the ion, but not the ion concentration, is considered to be involved in the free energy change in the cell, the normal electrode potential E_0 at the unit activity of the ion must be calculated by the equation

$$E = E_0 + \frac{RT}{2F} \ln m \gamma_{\text{Ni}^{++}} \quad (2)$$

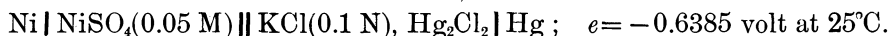
where $\gamma_{\text{Ni}^{++}}$ is the activity coefficient of the nickel ion at the molarity m of nickel sulphate.

Unfortunately, there are no data from which the activity coefficients of the nickel ion can be calculated. But, Lewis and Randall⁽¹⁾ have compiled a

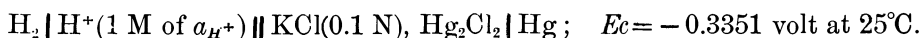
(1) Lewis and Randall, "Thermodynamics," (1923), p. 382.

table of the activity coefficients of individual ions at various ionic strengths by using certain assumptions. This table shows that the activity coefficients of ions of the same valency are nearly the same when the ionic strengths are not large. Therefore, without any other means for the time being until the actual measurements of the activity of the nickel ion can be made, an attempt was made to calculate the normal potential of nickel on the assumption that the activity coefficients of the nickel ion are the same as those of bivalent ions given in the table above cited. The necessary values at the ionic strengths used in this investigation were obtained by an interpolation or an extrapolation.

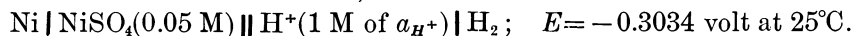
The electromotive force of the cell,



Taking Lewis and Randall's value of the potential of the decinormal calomel electrode⁽¹⁾.



By the combination of these two,



By a slight extrapolation from the table of activity coefficients of individual ions, we find the activity coefficient of bivalent metallic ion to be 0.24 at this concentration. Taking the activity coefficient of nickel ion for 0.05 M NiSO_4 as 0.24, we obtain for the above cell

$$-0.3034 = E_0 + 0.02958 \log 0.05 \times 0.24,$$

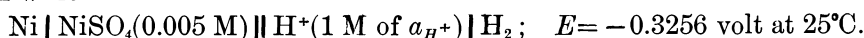
from which

$$E_0 = -0.2466 \text{ volt at } 25^\circ\text{C}.$$

The electromotive force of the cell



from which



The value of $\gamma_{\text{Ni}^{++}}$ at 0.005 M is 0.53. Substituting these values in equation (2),

$$-0.3256 = E_0 + 0.02958 \log 0.005 \times 0.53,$$

we obtain

$$E_0 = -0.2494 \text{ volt at } 25^\circ\text{C}.$$

As a mean value,

$$E_0 = -0.2480 \pm 0.0014 \text{ volt at } 25^\circ\text{C}.$$

Similarly, we may calculate E_0 at 18°C . For this purpose, however, it is necessary to evaluate the potential at 18°C . of decinormal calomel electrode referred to the standard hydrogen electrode.

The electromotive force measurements of the cell, $\text{H}_2 | \text{HCl}(0.1 \text{ M}), \text{Hg}_2\text{Cl}_2 | \text{Hg}$, by J. H. Ellis⁽²⁾ give -0.3978 volt at 18°C . Using this observed value, and taking 0.814 as the activity coefficient of 0.1 molal acid,

(1) Lewis and Randall, "Thermodynamics," (1923), p. 406.

(2) Ellis, *J. Am. Chem. Soc.*, **38** (1916), 754.

the electromotive force of the cell where both a_{H^+} and a_{Cl^-} are equal to unity can be calculated by the following equation.

$$-0.3978 = E_0 + \frac{RT}{F} \ln a_{H^+} a_{Cl^-} = E_0 + \frac{2RT}{F} \ln m a_{\pm}$$

$$E_0 = -0.3978 - 0.1853 \log 0.1 \times 0.814 = -0.2720 \text{ volt at } 18^\circ\text{C.}$$

From this value, the potential of the decinormal calomel electrode at 18°C. can be calculated by the equation

$$H_2 | H^+(1 \text{ M of } a_{H^+}) || KCl(0.1 \text{ N}), Hg_2Cl_2 | Hg; \quad E = E_0 - \frac{RT}{F} \ln \frac{1}{a_{Cl^-}}$$

Taking 0.794 as the activity coefficient of 0.1 molal $KCl^{(1)}$ and accordingly as that of chloride ion in the same solution, we obtain $E = -0.3355$ volt at 18°C. Combining this value with the results given in Table 3, E_0 of the nickel electrode at 18°C. can be calculated.

Let us first consider the cell

$Ni | NiSO_4(0.05 \text{ M}) || KCl(0.1 \text{ N}), Hg_2Cl_2 | Hg; \quad e = -0.6382$ volt at 18°C. ,
then, $Ni | NiSO_4(0.05 \text{ M}) || H^+(1 \text{ M of } a_{H^+}) | H_2; \quad E = -0.3027$ volt at 18°C.
By equation (2), $-0.3027 = E_0 + 0.02888 \log 0.05 \times 0.24$

$$E_0 = -0.2472 \text{ volt at } 18^\circ\text{C.}$$

Similarly, for the cell

$Ni | NiSO_4(0.005 \text{ M}) || KCl(0.1 \text{ N}), Hg_2Cl_2 | Hg; \quad e = -0.66105$ volt at 18°C.

$Ni | NiSO_4(0.005 \text{ M}) || H^+(1 \text{ M of } a_{H^+}) | H_2; \quad E = -0.32555$ volt at 18°C.

$$-0.32555 = E_0 + 0.02888 \log 0.005 \times 0.53$$

$$E_0 = -0.2511 \text{ volt at } 18^\circ\text{C.}$$

Consequently, as a mean value

$$E_0 = -0.2492 \pm 0.002 \text{ volt at } 18^\circ\text{C.}$$

For comparison, the values of normal electrode potentials calculated in the above are summarised in Table 4.

TABLE 4.
Values of normal electrode potential in volt.

	(1) Calculated from ion concentration.		(2) Calculated from ion activity.	
	25°C.	18°C.	25°C.	18°C.
From 0.05 M $NiSO_4$	-0.2503	-0.2509	-0.2466	-0.2472
From 0.005 M $NiSO_4$	-0.2489	-0.2507	-0.2494	-0.2511
Mean	-0.2496 ± 0.0007	-0.2508 ± 0.0001	-0.2480 ± 0.0014	-0.2492 ± 0.0002

It is important to have found out that, although the nickel electrodes are those which were prepared by reducing finely divided nickel oxide in an

(1) Lewis and Randall, "Thermodynamics," (1923), p. 362.

atmosphere of hydrogen, and probably some hydrogen was occluded in them, these values of E_0 calculated from the measurements with different concentrations are in perfect agreement with each other at the same temperature.

On the other hand, those values which were calculated from the activities of the ion of the two different concentrations are not so excellent agreement at both 18°C. and 25°C. as in the case of the values from the ion concentrations, though the difference amounts to only a few millivolts. This lack of agreement is probably due to the assumption involved in the calculation of activity of nickel ion. It is expected that more concordant results will be obtained if the activity of the nickel ion is measured accurately.

Change in Free Energy of Nickel Electrode Reaction. The change in free energy of the formation of nickel from its ion per equivalent, that is, $\frac{1}{2}Ni^{++} + \ominus = \frac{1}{2}Ni$, is expressed by the thermodynamic equation,

$$- \Delta F = E_0 F.$$

Taking as the values of E_0 at 25°C. -0.2496 volt which is the average of the normal electrode potential of nickel at one mol of ion concentration, we obtain,

$$\Delta F = 0.2496 \times 96500 / 4.182 = 5759 \text{ calories at } 25^\circ\text{C.}$$

In a similar way, taking -0.2508 volt as the mean value of E_0 at 18°C., we obtain,

$$\Delta F = 5787 \text{ calories at } 18^\circ\text{C.}$$

On the other hand, if we take the value of E_0 as -0.248 volt at 25°C. which is the average of the potentials at unit activity, then

$$\Delta F = 5723 \text{ calories at } 25^\circ\text{C.}$$

Similarly, from the value of -0.2492 volt at 18°C.

$$\Delta F = 5750 \text{ calories at } 18^\circ\text{C.}$$

These investigations were carried on under the direction of Professor G. Fuseya, with the aid of a grant made to him by the Saito Gratitude Foundation in Sendai, the writer wishes to express his great indebtedness, to him. The writer wishes to express his thanks also to Professor M. Katayama (Tokyo) for his counsel in several matters.

Summary.

1. A reproducible electrode, which gives a constant and reversible potential of active nickel was obtained by using powdered nickel reduced with hydrogen directly in the cell and also using an apparatus which allows the cell to be filled with the electrolyte entirely in the absence of air.

2. The potentials of the reduced nickel powder in 0.05 M and 0.005 M nickel sulphate solutions both at 25°C. and 18°C. were measured in an atmosphere of hydrogen.

3. The normal electrode potentials of nickel were calculated from these observed potentials on the ground of two different concepts of the strong electrolytes, one being that the ion concentrations calculated from the conductance viscosity ratios are involved in the expression of the electromotive force of a concentration cell and the other being that the ion activities are involved. The average values of these normal electrode potentials are -0.2496 volt ($25^{\circ}\text{C}.$) and -0.2508 volt ($18^{\circ}\text{C}.$) at one molal ion concentration, and -0.2480 volt ($25^{\circ}\text{C}.$) and -0.2492 volt ($18^{\circ}\text{C}.$) at one molal ion activity.

4. The change in free energy of nickel electrode reaction per equivalent, that is, $\frac{1}{2}\text{Ni}^{++} + \ominus = \frac{1}{2}\text{Ni}$ was calculated from the above electrode potentials.

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ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS
PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES
IN JAPAN⁽¹⁾. I. THE AKITA HOKUTOLITE.

By Ichizo SUGANUMA.

Received February 4, 1928. Published March 28, 1928.

The Constituents and Genesis of the Akita Hokutolite Produced from a Sulphurous Hot Spring called Shikayu in Akita Prefecture. A heavy crystalline mineral produced from a sulphurous spring in Akita-ken, a province of Japan, is very similar in its appearance and properties to hokutolite from the Hokuto Spring in Taiwan i. e. Formosa.⁽²⁾ Some mineralogists of this country supposed that the former mineral is of the same kind as the latter, but this not being proved by any accurate experiments, the author analysed and examined the former mineral, and has obtained the result that it is of the same kind as hokutolite. Therefore the author thinks that the mineral can properly be called the *Akita hokutolite*. The chief constituents of the Akita hokutolite are BaSO_4 and PbSO_4 , and the mineral consists of the isomorphous mixture of the above constituents just as the Taiwan hokutolite does, but the former differs from the latter in the following points:—

(1) The different samples of the Akita hokutolite vary in a wide range in their compositions i. e. the ratios of BaSO_4 and PbSO_4 contained in them,

(1) Read before the Chemical Society of Japan, July 11, 1922.

(2) Okamoto, *J. Geol. Soc. Tokyo*, 18 (1911), 19; *Beitr. Mineral. Japan*, 4 (1912), 178; Hayakawa and Nakano, *Z. anorg. Chem.*, 78 (1912), 183; Richards and Sameshima, *J. Am. Chem. Soc.*, 42 (1920), 928.

while the composition of the Taiwan hokutolite is approximately constant.

(2) Generally, BaSO_4 predominates in the former mineral than in the latter, and sometimes is nearly equal to a mineral barite.

(3) The Taiwan hokutolite is always of brown colour, while the Akita hokutolite is sometimes of light yellow or even white, besides the ordinary kind of brown colour.

(4) As a remarkable difference, the accompanying rare elements of the Akita hokutolite are much greater in kinds than those reported on the Taiwan hokutolite, especially, the radioactivity of the mineral is not only ascribed to the radio-active elements of radium series but to the radio-active elements of thorium series, because the presence of thorium and its active deposits has been proved by the chemical analysis and the radioactive experiments.

(5) The commonest kind of the Akita hokutolite is composed from a great number of small rhombic brownish crystals as the Taiwan hokutolite, but the former contains thin white layers in regular intervals i. e. a zonal structure of the two layers of brown and white, while such two different layers are not clearly perceived in the latter mineral.

The author separated the two layers of the Akita hokutolite from each other and analysed each layer in order to find out the difference between the compositions of the two layers.

The results of the analysis show that in the white layer BaSO_4 is much greater than in the brownish layer, and also SiO_2 is somewhat greater, while in the brownish layer predominate PbO and FeO as PbSO_4 and probably $\text{PbS}_5\text{O}_6 \cdot x \text{FeS}_6\text{O}_6$. The author ascribes the brownish colour of the mineral to pentathionate of Pb and Fe from several experimental facts.

The ordinary metallic elements contained as impurities in the Akita hokutolite are Sr, Ca, Mg of Ba group with Al and Fe; and further the presence of the rare metallic elements such as Ti, Zr, Th, Ce, La, Pd and Nd, and Ra, Rn, Po of U series has been determined qualitatively (but some quantitatively) in the mineral.

Among these, the presence of Th has been ascertained by the analytical results and by tracing the decay curve of active deposits of Th emanation, but radium accompanying Ba salts in a very minute quantity is proved only by the radio activity of the solid salts and by determining half period of radium emanation evolved from the solution of those salts.

As to uranium, the mother element of radium, the author could only find a trace of it by the colour reaction with $\text{K}_4\text{Fe}(\text{CN})_6$, but polonium, one of the transformation products of radium, could easily be detected by its characteristic chemical reactions and by plotting the decay curve particular to the metallic film of Po deposition on the bismuth plate.

Therefore, the radio activity of the Akita hokutolite is due to the several radio active elements belonging to radium series and thorium series.

In regard to the genesis of the Akita hokutolite, the author has found the facts that it is deposited only on the rock surface which is covered or washed by the spring water cooled to the temperature of 40°C. and that this temperature highly favours the growth of Cyanophyceae, and further that the gelatinous matter contained in these Cyanophyceae causes the coagulation of silicic acid hydrosol from the acidic solution containing aluminium ion just as the ordinary gelatine or albumen does.

Thus the author has come to assume that the components of the hokutolite come gradually to coat the rock surface by the aid of the silicic acid hydrogel.

In regard to the zonal structure of the hokutolite i. e. white and brown layers, the author considers that the white layer, which is mostly composed of matters with very insoluble properties such as BaSO_4 , is formed by a current of the strongest acidity and also of the highest temperature.

Such an acidity and temperature can exist only with the smallest supply of the river water in the coldest season.

Pentathionate and sulphide of lead and iron are almost dissolved by such a hot acidic current. Thus we have a white layer and a white deposition. Sometimes in this season, the upper dried part of the rock above the surface of the current, exposes Cyanophyceae to the coldest atmospheric air and destroys the vegetable constitutions, leaving behind a gelatinous or slimy matter. The rock surface naturally absorbs the splashes of the river water and coagulates silicic acid hydrosol contained in them.

This conclusion on the formation of the white layer in the coldest season is pretty well confirmed by the surfaces of those samples which the author collected in that season.

In regard to the brown layer of the hokutolite, the gelatinous matter produced by the natural metabolism of Cyanophyceae first coagulates silicic hydrosol and gradually adsorbs more and more of those brown components insoluble in the warm dilute acid.

Besides, the author observes about some other specimens that Cyanophyceae are totally destroyed by the cold flood of melted snow in the spring season. In most of these cases, the gelatinous matter contained, cooperates with the aluminium ion in the river current in coagulating the silicic hydrosol forming a muddy brown deposition. In either of these cases, the brown layer contains a comparatively larger proportion of lead and iron compounds soluble in acid water at a higher temperature than 40°C.

In fact the sample of the Akita hokutolite collected in the lowest part of the current contains the largest proportion of lead, but that collected in the vicinity of the source of the spring the smallest proportion of lead and iron as shown by the Table 2.

The latter sample, which is very near to barite in its composition, appears to have been deposited upon rocks exposed out of the river surface, the hot water splashing out energetically from a certain spring, having been cooled down. It is probable that these depositions have been cemented by the colloidal silicic acid precipitated first, because when the hot water of the spring source is collected in a beaker and allowed to cool for a while, the clear liquid gradually becomes cloudy and precipitates colloidal silicic acid hydrogel as has been observed by the author.

The following tables show the compositions of the white and brown layers in the Akita hokutolite compared (Table 1), and the compositions of the samples collected in the vicinity of the spring source and at the lowest part of the river current (Table 2), as well as the composition of the spring source itself (Table 3).

TABLE 1.

Compositions of the white and brown layers of the Akita hokutolite :

Component	White layer	Brown layer	Component	White layer	Brown layer
PbO	6.45	9.72	K ₂ O	0	0
BaO	55.33	53.80	Na ₂ O	—	—
SrO	0.11	0.08	SiO ₂	4.61	2.53
CaO	0.34	0.32	SO ₃	31.43	32.19
MgO	0.25	0.25	As ₂ O ₅	(0.01)	—
Fe ₂ O ₃ (CeO ₂ , ThO ₂ , etc.)	0.43	0.54	NH ₄ Cl	—	(0.02)
Al ₂ O ₃	0.52	0.47	total	99.48 %	99.92 %

TABLE 2.

Compositions of the samples collected in the vicinity of the spring source and at the lowest part of the hot river current :

Component	Sample at the upper part of the spring.	Sample at the lowest part of the river.	Component	Sample at the upper part of the spring.	Sample at the lowest part of the river.
BaO	62.18	48.47	MgO	—	0.20
PbO	4.61	15.04	SiO ₂	0.44	3.28
Fe ₂ O ₃ }	0.26	0.52	SO ₃	32.49	30.31
Al ₂ O ₃ }			total	99.98 %	98.20 %
CaO	—	0.38			

TABLE 3.

Composition of the spring source called Akita Shikayu.
(1000 parts taken ; temperature of the spring 97°C., strong acid.)

BaSO ₄	0.0011	NaCl	0.1121
PbSO ₄	0.0009	NH ₄ Cl	0.0003
FeSO ₄	0.1832	HCl	2.5497
Al ₂ (SO ₄) ₃	0.8610	H ₂ SO ₄	0.4247
CaCl ₂	0.0033	H ₂ SiO ₃	0.3436
MgCl ₂	0.0581	H ₃ BO ₃	tr.
AsCl ₃	0.0027	ZrCl ₄	tr.
KCl	0.0752		

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ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS
PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES
IN JAPAN. II. COMPOSITION AND GENESIS OF
SOLUBLE SULPHATES PRODUCED IN THE
ENVIRONMENTS OF A SULPHUROUS SPRING.

By Ichizo SUGANUMA.

Received February 4, 1928. Published March 28, 1928.

The so-called sulphurous gas gushing out from the cavities which are located in a region of sulphurous spring, chiefly consists of H_2S , CO_2 , and steam or vapour. If the gas contains steam or vapour in a large amount, the temperature of the gas mostly attains about 100 degrees.

The sulphurous gas above explained, gushing from the fissure of the andesite rock or the cavity of clay which is formed by the decomposition of the andesite, gradually acts physically and chemically on the surface of the rock or clay above mentioned.

As the result of these action, a long needle-like crystalline efflorescence of white or light yellow with a silky appearance, is deposited on the surface.

An alum spring in the vicinity of Beppu in Oita-ken, a province of Kyushu, Japan, gives us a large amount of these crystalline masses by the natural production above mentioned, and in Nasu-Motoyu in the vicinity of Nikko, and also in Owaku-dani in Hakone. These natural crystalline products are collected and utilized for both bathing and medical purposes.

These crystals under microscope have a fibrous structure mostly with a few opaque nodes as on grasses, generally white in colour, but sometimes of light yellowish white, or yellow, or even mixed with yellowish powder of native sulphur.

The needle-like, silky white crystals, which are of the commonest kind, have a melting point $105^{\circ}\text{C}.$, are soluble in water, and the aqueous solution of them is strongly acid.

The composition of the crystals is $\text{Al}_2(\text{SO}_4)_3$ and FeSO_4 , and contains the same molecules of water of crystallization as in the common alum. In mineralogy, these crystals are called *halotrichite*.

The author obtained these crystals experimentally by passing steam mixed with H_2S and CO_2 on the Hakone andesite finely powdered and well washed, and on another experiment obtained the same result by passing steam through the andesite powder which was percolated with a dilute H_2SO_4 , and allowing it to stand on a glass plate for a few days.

Therefore we know that the genesis of the crystals above mentioned is due to the weathering action of aluminium silicate and iron silicate contained in the andesite by carbonic acid or the other acids, and at the same time, to the formation of aluminium sulphate and iron sulphate by the action of H_2SO_4 produced by the oxidation of H_2S .

In the same region of sulphurous spring that produces halotrichite, there are found other snow-white crystalline masses similar in appearance to the above mineral.

These crystals under a microscope are found to be transparent, colourless and scaly, and they have a melting point $115^{\circ}\text{C}.$

The composition obtained by chemical analysis corresponds to $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ i.e. a mineral called *alunogen* mineralogically. The author observed certain samples which consist of halotrichite on the top and of alunogen on the base, and sometimes observed the facts that alunogen is chiefly formed on clay longly exposed to air and sulphurous gas and fully decomposed by acids.

On these facts it is supposed that alunogen is formed from the clay poor in iron, subjected under the action of sulphurous gas, while the clay at first rich in iron, produces halotrichite.

Furthermore, the author observed the existence of light green crystalline masses as efflorescence on a black volcanic rock in Taiwan or some dark green clay in Fukeno-yu, Akita prefecture. The formation of these crystals is probably due to the action of sulphurous gas on rocks or clay very rich in iron, and the composition and properties of the crystals correspond to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ i.e. native green vitriol or *melanterite* in mineralogy. The fact that the samples of these crystals are frequently contaminated with halo-

trichite when tested under a microscope, is easily accounted for by the above reasoning of their formation.

Now, rocks with melanterite and halotrichite formed on their surfaces, are found to contain some fine crystalline particles of FeS_2 i. e. iron pyrites in their small cavities. Probably this is the case of the formation of FeS_2 by the interaction of hydrogen sulphide and iron silicate in the absence of air.

The author has frequently observed the fact that gypsum exists on a rock surface where the steam in sulphurous gas is gradually condensed. This mineral is, no doubt, formed from calcium silicate contained in rocks by the action of H_2SO_4 , which is an oxidized product of H_2S .

It is a noticeable fact that a sulphurous gas containing only a small proportion of water vapour and naturally dry gas mixture composed of H_2S and CO_2 of ordinary temperature, frequently acts as a very poisonous gas as war gas. Some examples of this are found in the sulphurous gas in Sessho-seki in Nasu, and Sessho-dani in Akita Shika-yu, Akita Prefecture, Japan.

TABLE 1.
Analytical results of alunogen.

Component	Observed value	Calc. value as $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$
Al_2O_3	16.17	16.22
FeO	tr.	—
MgO	tr.	—
CaO	0.30	—
SO_3	38.01	38.09
H_2O	45.13 (at $325^\circ\text{C}.$)	45.69
SiO_2 (in sol. in acids)	0.23	—
total	99.84	100.00

TABLE 2.
Analytical results of halotrichite.

Component	Observed value	Calc. value as $\text{Al}_2(\text{SO}_4)_3 \cdot \text{FeSO}_4 \cdot 24\text{H}_2\text{O}$
Al_2O_3	10.28	11.03
FeO	8.56	7.75
MgO	0.12	—
CaO	0.46	—
SO_3	34.85	34.56
H_2O	44.82 (at $325^\circ\text{C}.$)	46.66
SiO_2 (insol. in acids)	1.24	—
total	100.33	100.00

TABLE 3.
Analytical results of melanterite.

Component	Observed value	Calc. value as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
FeO	25.25	25.90
Al_2O_3	2.12	—
CaO	0.46	—
MgO	0.36	—
SO_3	27.65	28.77
H_2O	—	45.33
total	—	100.00

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ON THE OXIDATION OF SODIUM SULPHITE IN SODIUM CARBONATE SOLUTION WITH AIR.

By Susumu MIYAMOTO.

Received February 8, 1928. Published March 28, 1928.

In connection with the former study on the effect of sodium hydroxide on the oxidation of sodium sulphite⁽¹⁾ with air, the present research was carried out under the same condition, expecting that it will be able to calculate the dissolution velocity of oxygen into sodium carbonate solution from the result.

The experimental procedure was quite the same as that described in the previous paper⁽²⁾. In the following tables, v is the volume of sodium thio-sulphate solution of 0.0996 normal, which is equivalent to the quantity of sodium sulphite; k was calculated by $k = \frac{1}{t}(v_0 - v)$, v_0 being the value of v at $t = 0$; $v_{calc.}$ was obtained by $v_{calc.} = v_0 - kt$, using the mean value of k . The value of k , when $C_{Na_2CO_3} = 0$, given in the following tables, is that obtained in the previous study⁽³⁾.

(1) S. Miyamoto, this journal, 2 (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 40.

(2) Ibid.

(3) Ibid.

TABLE 1.

Temp.=20°C. Velocity of air=7.78 litres per hour.

$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k	$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k	
0	—	—	—	0.330	0.0750	0	18.08	—	—	
0.01875	0	23.57	—	—		10	15.61	15.59	0.247	
	10	20.81	20.72	0.276		25	12.01	11.85	0.243	
	25	16.43	16.44	0.286		50	6.05	5.63	0.241	
	50	9.14	9.32	0.289		0	11.58	—	—	
	0	19.24	—	—		9	9.39	9.34	0.243	
	10	16.48	16.39	0.276		20	6.58	6.60	0.250	
	20	13.22	13.54	0.301		Mean: 0.249				
	40	6.99	7.84	0.306		0.1875	0	22.77	—	—
	0	14.62	—	—			10	20.32	20.39	0.245
	10	11.84	11.77	0.278	25		16.61	16.82	0.246	
20	9.13	8.92	0.275	55	9.47		9.68	0.242		
35	4.50	4.64	0.289	0	15.14		—	—		
0	11.31	—	—	10	12.74		12.76	0.240		
9	8.78	8.74	0.281	25	9.14		9.19	0.240		
15	7.04	7.03	0.285	50	4.33		3.24	0.216		
25	4.45	4.18	0.274	0	12.44		—	—		
Mean: 0.285				9	10.26		10.30	0.242		
0.0375	0	22.53	—	—	20	7.49	7.68	0.248		
	10	19.82	19.89	0.271	35	4.50	4.11	0.227		
	20	17.13	17.25	0.270	Mean: 0.238					
	50	9.12	9.33	0.268	0.2625	0	20.21	—	—	
	0	20.81	—	—		10	17.82	17.94	0.239	
	10	18.16	18.17	0.265		25	14.40	14.53	0.232	
	20	15.81	15.53	0.250		55	7.50	7.72	0.231	
	50	7.20	7.61	0.272		0	14.32	—	—	
	0	16.15	—	—		10	11.97	12.05	0.235	
	10	13.48	13.51	0.267		25	8.64	8.64	0.227	
20	10.94	10.87	0.261	0		13.49	—	—		
45	4.80	4.27	0.252	10		11.21	11.22	0.228		
Mean: 0.264				25		7.96	7.81	0.221		
0.0750	0	18.91	—	—	0.3750	0	19.18	—	—	
	10	16.34	16.42	0.257		10	16.95	16.97	0.223	
	25	12.42	12.68	0.260		25	13.75	13.65	0.217	
	50	6.36	6.46	0.251		55	7.20	7.58	0.218	

TABLE 1. (Continued.)
Temp.=20°C. Velocity of air=7.78 litres per hour.

$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k	$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.3750	0	19.00	—	—	0.938	0	19.61	—	—
	10	16.72	16.79	0.228		15	17.39	17.36	0.148
	25	13.31	13.47	0.228		30	15.11	15.11	0.150
						60	10.36	10.61	0.154
	0	14.53	—	—		0	14.39	—	—
	10	12.33	12.32	0.220		15	12.22	12.14	0.145
	25	8.94	9.00	0.224		30	10.09	9.89	0.143
	45	5.22	4.58	0.207		60	5.05	5.39	0.156
	Mean: 0.221					Mean: 0.150			
	0.563	0	22.20	—		—	1.125	0	23.95
15		19.41	19.38	0.186	10	22.58		22.62	0.137
30		16.76	16.56	0.181	25	20.61		20.62	0.134
					50	17.25		17.30	0.134
0		21.82	—	—	0	22.88		—	—
10		19.84	19.94	0.198	15	20.89		20.88	0.133
25		16.92	17.12	0.196	30	18.92		18.89	0.132
55		11.40	11.48	0.189	60	14.57		14.90	0.139
0		14.47	—	—	0	14.17		—	—
15		11.74	11.65	0.182	15	12.37		12.17	0.120
30		8.82	8.83	0.188	30	10.24		10.18	0.131
55		4.58	4.13	0.180	60	5.97		6.19	0.137
Mean: 0.188				Mean: 0.133					
0.750		0	24.77	—	—	1.313		0	28.49
	10	23.06	23.12	0.171	25		25.29	25.41	0.128
	30	19.60	19.82	0.172	50		22.49	22.34	0.120
	60	14.37	14.87	0.173					
	0	23.93	—	—	0		25.08	—	—
	10	22.30	22.28	0.163	25		21.80	22.00	0.131
	25	19.79	19.80	0.166	50		18.97	18.93	0.122
	60	14.33	14.03	0.160					
	0	14.75	—	—	0		14.99	—	—
	15	12.29	12.27	0.164	15		13.27	13.14	0.115
	30	9.79	9.80	0.165	30		11.45	11.30	0.118
	60	5.57	4.85	0.153	55		8.47	8.22	0.119
	Mean: 0.165				0		12.34	—	—
	0.938	0	25.63	—	—		15	10.31	10.49
15		23.30	23.38	0.155	30	7.74	8.65	0.120	
30		21.18	21.13	0.148	55	5.83	5.57	0.118	
60		16.63	16.63	0.150	Mean: 0.123				

The Effect of Sodium Carbonate. Table 1 shows that the oxidation velocity of sodium sulphite in sodium carbonate solution decreases with the increase of the concentration of the latter, quite the same way as in the case of its oxidation in sodium hydroxide solution. The velocity constant seems to be expressed as a linear function of $C_{\text{Na}_2\text{CO}_3}$, when $C_{\text{Na}_2\text{CO}_3}$ is greater than about 0.02 normal; $k_{\text{calc.}}$ in Table 3 was calculated by $k_{\text{calc.}} = 0.258 - 0.114 C_{\text{Na}_2\text{CO}_3}$.

TABLE 2.
Velocity of air = 7.78 litres per hour.

Temp.	$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k
30°C.	0.1875	0	22.28	—	—
		10	19.48	19.57	0.280
		25	15.25	15.50	0.281
		55	7.42	7.37	0.270
		0	15.52	—	—
		10	12.96	12.81	0.256
		20	10.18	10.10	0.267
		40	4.62	4.68	0.273
		Mean: 0.271			
		0	24.77	—	—
		10	22.26	22.28	0.251
		30	17.47	17.30	0.243
		60	9.85	9.83	0.249
		0	15.78	—	—
		10	13.28	13.29	0.250
30°C.	0.3750	20	10.76	10.80	0.251
		45	4.67	4.57	0.247
		Mean: 0.249			
		0	29.33	—	—
		10	27.53	27.62	0.180
		30	23.89	24.20	0.181
		60	18.95	19.07	0.173
		0	14.51	—	—
		15	12.10	11.94	0.161
		30	9.47	9.38	0.168
		60	4.13	4.25	0.173
		0	12.17	—	—
		15	9.73	9.60	0.163
		30	7.23	7.04	0.165
		55	2.77	2.76	0.171
		Mean: 0.171			

TABLE 2. (Continued.)
Velocity of air=7.78 litres per hour.

Temp.	$C_{\text{Na}_2\text{CO}_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
40°C.	0.1875	0	23.96	—	—
		10	21.06	21.08	0.290
		25	16.51	16.76	0.298
		55	8.29	8.12	0.285
		0	15.33	—	—
		10	12.44	12.45	0.289
		20	9.61	9.57	0.286
		40	4.05	3.81	0.282
		Mean: 0.288			
40°C.	0.3750	0	22.82	—	—
		15	18.68	18.93	0.276
		30	15.03	15.05	0.260
		60	7.53	7.28	0.255
		0	15.94	—	—
		10	13.33	12.35	0.261
		20	10.91	10.76	0.252
		45	4.69	4.28	0.250
		Mean: 0.259			
40°C.	0.938	0	23.67	—	—
		15	20.97	20.82	0.180
		30	17.68	17.97	0.200
		60	11.96	12.27	0.195
		0	14.15	—	—
		15	11.17	11.30	0.199
		30	8.75	8.45	0.180
		55	3.90	3.70	0.186
		Mean: 0.190			

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are given in Table 2. The effect of temperature was small, as can be expected.

$$\begin{aligned}
 \frac{k_{30^\circ}}{k_{20^\circ}} &= \frac{0.271}{0.238} = 1.14, & \frac{k_{40^\circ}}{k_{30^\circ}} &= \frac{0.288}{0.271} = 1.06 & \text{when } C_{\text{Na}_2\text{CO}_3} &= 0.1875 \text{ N.} \\
 \frac{k_{30^\circ}}{k_{20^\circ}} &= \frac{0.249}{0.221} = 1.13, & \frac{k_{40^\circ}}{k_{30^\circ}} &= \frac{0.259}{0.249} = 1.04 & \text{when } C_{\text{Na}_2\text{CO}_3} &= 0.3750 \text{ N.} \\
 \frac{k_{30^\circ}}{k_{20^\circ}} &= \frac{0.171}{0.150} = 1.14, & \frac{k_{40^\circ}}{k_{30^\circ}} &= \frac{0.190}{0.171} = 1.11 & \text{when } C_{\text{Na}_2\text{CO}_3} &= 0.938 \text{ N.}
 \end{aligned}$$

TABLE 3.

Temp.	$C_{\text{Na}_2\text{CO}_3}$ normal	k	$k_{\text{calc.}}$	Dissolution velocity of oxygen mols per minute.
20°C.	0	0.330	—	8.2×10^{-6}
	0.01875	0.285	0.256	7.1 „
	0.03750	0.264	0.254	6.6 „
	0.0750	0.249	0.249	6.2 „
	0.1875	0.238	0.237	5.9 „
	0.2625	0.227	0.228	5.7 „
	0.3750	0.221	0.215	5.5 „
	0.5630	0.188	0.194	4.7 „
	0.750	0.165	0.172	4.1 „
	0.938	0.150	0.151	3.7 „
	1.125	0.133	0.130	3.3 „
	1.313	0.123	0.108	3.1 „
30°C.	0	0.345	—	8.6 „
	0.1875	0.271	—	6.7 „
	0.3750	0.249	—	6.2 „
	0.938	0.171	—	4.3 „
40°C.	0	0.382	—	9.5 „
	0.1875	0.288	—	7.2 „
	0.3750	0.259	—	6.4 „
	0.938	0.190	—	4.7 „

The Dissolution Velocity of Air. As was expected, the oxidation velocity of sodium sulphite in sodium carbonate solution was independent of its concentration under the condition of this experiment. The result can be explained by the assumption that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen into sodium carbonate solution. The dissolution velocity, given in Table 3, is that of oxygen, when air was passed into 40 c.c. of sodium carbonate solution in a test tube (diameter $\div$ 3 cm.) through a glass tube (inside diameter $\div$ 4 mm., outside diameter $\div$ 6 mm.) at the rate of 7.78 litres per hour, and was calculated from the value of k . The dissolution velocity of oxygen into sodium carbonate solution seems to be a little smaller than that into sodium hydroxide solution, obtained in the previous study⁽¹⁾.

(1) S. Miyamoto, this journal, 2 (1927), 158; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 192.

Summary.

(1) The oxidation velocity of sodium sulphite in sodium carbonate solution of various concentrations was observed. The oxidation velocity was independent of the concentration of sodium sulphite under the condition of the present experiment, and the velocity constant was expressed as a linear function of the concentration of sodium carbonate approximately, when $C_{\text{Na}_2\text{CO}_3}$ is greater than about 0.02 normal.

(2) The effect of temperature was small.

(3) The dissolution velocity of oxygen into sodium carbonate solution of various concentrations was obtained indirectly.

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THE SYSTEMS HYDROGEN CHLORIDE—ETHYL ETHER
AND HYDROGEN CHLORIDE—ACETONE.

By D. McINTOSH.

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In 1904, Archibald and McIntosh⁽¹⁾ published the results of an investigation of the compounds produced by the addition of the halogen hydrides to organic substances containing oxygen. They isolated a compound of hydrogen chloride and ether, melting at -92° , which had the composition $C_4H_{10}O-5HCl$. This ratio was fixed by two methods. The liquefied acid was "titrated" with ether at the same temperature, and a point was found, corresponding to the ratio of five molecules to one, where the further addition of ether developed very little heat, while before that amount of ether was added, any addition occasioned a considerable heat evolution. By a second method, in which a serious error could hardly be made, the compound was separated, dried at low temperature and analysed. The results showed that the compound corresponded closely to the formula $C_4H_{10}O-5HCl$.

Maass and McIntosh⁽²⁾ investigated the system ether—hydrogen chloride. They found that the three compounds $C_4H_{10}O-HCl$, $2HCl$ and $5HCl$

(1) *J. Chem. Soc.*, **85** (1904), 919.

(2) *J. Am. Chem. Soc.*, **35** (1913), 535.

existed, so that this system was more complicated than that of the methyl ether and acid, examined by them and by Baume⁽¹⁾. In 1926 Hirai⁽²⁾ repeated this work, and concluded that but one compound, $C_4H_{10}O \cdot 2HCl$, was formed. As these oxonium compounds have a new interest on account of the development of the electron theory of valence, I have re-examined certain parts of this system. The results show the formation of three compounds mentioned above.

Materials and Apparatus. The ether and acetone were purified and dried by sodium and calcium chloride, respectively. The hydrogen chloride was made by the action of strong sulphuric acid on hydrochloric acid. It was dried by sulphuric acid and phosphoric anhydride.

The apparatus is shown in the sketch. It consisted of a double-walled freezing-point tube, closed by a rubber stopper. This contained a magnetic stirrer and a resistance thermometer. Two glass tubes passed through the stopper; one reaching to the bottom served to introduce the gaseous acid. The solutions were made by weight, all weighings being made at low temperature. We have shown in previous papers that this can be done to 0.1 per cent.

A Heraeus platinum-quartz thermometer with a resistance of 25.031 ohms and a Leeds and Northrup bridge were used. The thermometer was tested at the carbon dioxide temperature, at the freezing temperature of acetone (-94.6°), and at the temperature of boiling oxygen. Immediately before or after each series of measurements its resistance at -94.6° or -78.5° was determined.

The solutions were cooled by a bath of carbon dioxide and ether boiling under reduced pressure. It was an easy matter to keep the temperature of the bath within a few degrees of the freezing-point of the solution.

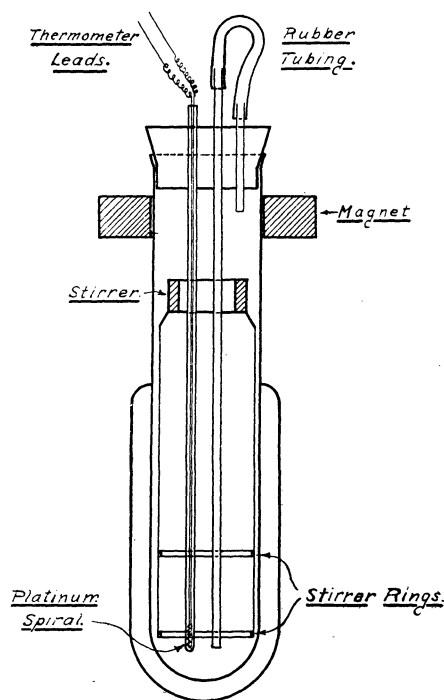


Fig. 1.

(1) *Arch. Science physiques*, **33** (1912), 415.

(2) This journal, **1** (1926), 123.

TABLE 1.

Experiment	Mols. per cent. Acid.	Freezing-point.	Experiment	Mols. per cent. Acid.	Freezing-point.
1.	42.5	-102.9°	5.	67.6	-83.2°
	47.3	-100.0		70.0	-84.8
	56.5	-100.4		.	.
2.	53.2	- 98.9	6.	80.5	-99.6
		- 98.9		83.6	-92.9
		- 98.9		85.0	-94.2
3.	50.0	- 98.6	7.	81.5	-96.2
	68.6	- 83.2		85.0	-94.2
4.	46.7	-101.3	8.	53.7	-99.5
	54.2	- 97.9		67.6	-82.8
	65.9	- 82.0			
	68.6	- 83.2	9.	66.4	-82.0
	71.6	- 97.6			
5.	50.6	- 99.7	10	84.5	-92.6

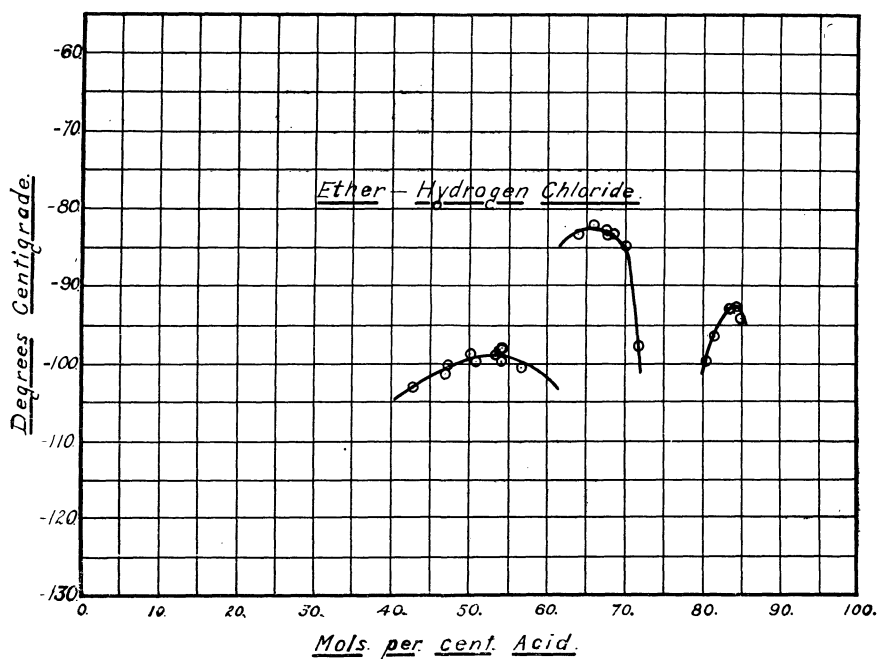


Fig. 2.

The results are shown in Table 1 and on the curve, and indicate the formation of the three compounds found by Maass and McIntosh. The

general form of the curves is the same in the two investigations, but the individual points differ rather widely. From the irregularities in my results an experimental error of about two degrees may be assumed.

The difference in our results is due, I think, to Hirai's failure to realize the difficulty of precipitating compounds from the supercooled liquids. Maass and McIntosh⁽¹⁾ say: "Avoiding too vigorous agitation it is quite possible to maintain the ethers and alcohols in liquefied hydrochloric acid as solutions many degrees below their real freezing-points. The phenomenon of supercooling is particularly well seen in all these oxonium compounds"; and I have repeatedly kept these mixtures at ten degrees below their true freezing-points for five hours at a time, agitating meanwhile with the magnetic stirrer, without precipitation taking place.

It is possible, however, to bring about crystallisation at any temperature below the freezing-point by "inoculating" the solution with a minute amount of the ether-hydrogen chloride or bromide complex introduced by means of a capillary tube. The crystals of the latter are made up of a mixture of $C_4H_{10}O \cdot HBr$ and $C_4H_{10}O \cdot 2HBr$,⁽²⁾ and bring about a separation of the one and two hydrogen chloride salts, with a consequent rise in temperature, so that determinations can be made with any desired degree of accuracy. These salts have no influence on the precipitation of the $5HCl$ compound; that must be brought about by vigorous stirring and low temperature.

The System Acetone—Hydrogen Chloride. Archibald and McIntosh made and analysed a compound containing two molecules of acetone to five of acid. The examination of this system by Hirai yielded only one compound, $C_3H_6O \cdot HCl$. I have therefore determined a few points on the freezing-point curve, and these show that both compounds are formed. The results are given in Table 2 and are shown on the curve. They are in fair agreement with Hirai's up to sixty mols. per cent. acid.

TABLE 2.

Mols. per cent. Acid.	Freezing-point.	Mols. per cent. Acid.	Freezing-point.
36.5	-91.5°	69.7	-81.2°
47.1	-76.9	71.7	-80.8
54.0	-78.0	74.3	-85.3
57.7	-84.6	53.8	-78.0
63.2	-94.6		

(1) *J. Am. Chem. Soc.*, loc. cit.

(2) McIntosh, *ibid.*, 33 (1911), 71; Maass and McIntosh, *ibid.*, 34 (1912), 1273.

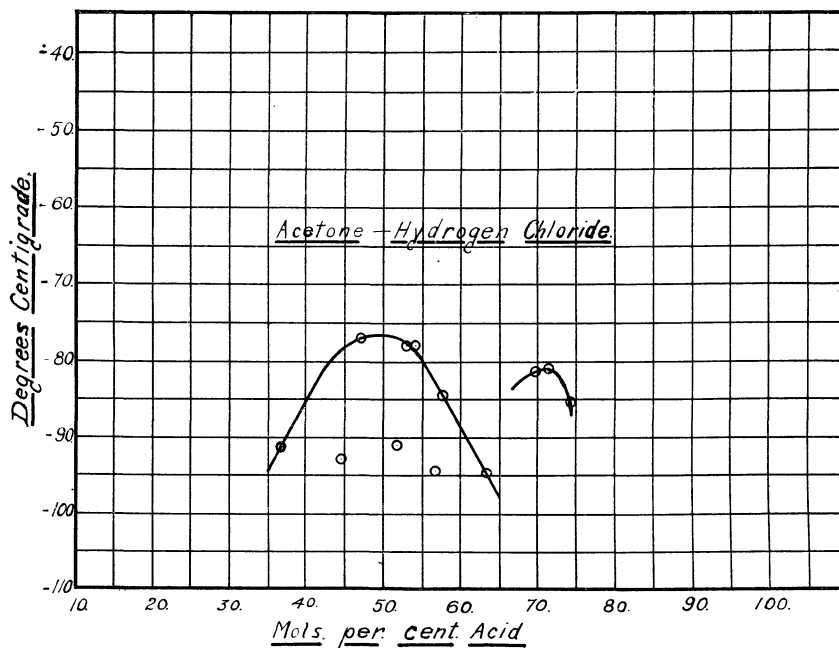


Fig. 3.

What has been said of the ether-hydrogen chloride system applies with equal force to the acetone one. The separation of the first compound takes place on the addition of the acetone-hydrochloric or acetone-hydrobromic complex; the other compound is not precipitated in this way; it is formed by cooling the solution and stirring.

The freezing-point (-79°) given by Hirai for his compound is too low. I have kept the solid crystallized from 50.1 mols. per cent. acid at -78.5° for 20 hours without melting taking place.

On the diagram three points inside the curve are shown. These points were obtained when a chalky precipitate, quite different in appearance from either of the two compounds, separated. On re-melting and repeating the observation the result fell on the curve. This may mean a new compound which separates from the solution as does the heptahydrate of sodium sulphate from a supersaturated solution of the decahydrate when the system is cooled to a fairly low temperature.

Finally, an acetone-hydrogen chloride solution containing for more than sixty mols. per cent. acid does not become viscous if kept only a degree or two below its true freezing-point. If cooled to a low temperature it naturally forms a glass.

September, 1927.

Dalhousie University,
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ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS
PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES
IN JAPAN. III. CALCIUM CARBONATE MINERALS
DEPOSITED FROM EFFERVESCENT SPRINGS.

By Ichizo SUGANUMA.

Received February 4, 1928. Published April 28, 1928.

Calcium carbonate when deposited from effervescent springs in Japan, rarely forms a transparent colourless mineral, and in most cases an opaque-light-yellow crystalline mass. The latter is frequently contaminated with oxide of iron, sometimes mixed with oxide of manganese, silicic acid, arsenious sulphide etc. Therefore, in almost all cases, the mineral when treated with hydrochloric acid, is reduced to a small insoluble portion, while the larger proportion is dissolved with effervescence.

The mineral presents various forms and appearances, namely, a massive rock, an earthy mass, a small spherical globule, a long fibrous or sometimes white silky crystalline mass, an oolitic group etc. Which of these forms belong to aragonite or calcite, can hardly be distinguished by ordinary optical tests, though the former crystallises in a rhombic system, and the latter in a hexagonal system. At present X-ray analysis is used for the determination of crystalline system, but the apparatus employed being very complex, we often prefer a simpler but pretty accurate method. As is well known, aragonite is greater than calcite in its specific gravity, but it is difficult to estimate its value, for the mineral is of porous structure. Therefore, the author considers that the method discovered by Meigen⁽¹⁾ is most simple and reliable, and he has applied this method to several CaCO_3 minerals for the classification of them.

On the author's experiments, calcium carbonate precipitated at a temperature higher than 50°C . forms aragonite, but at a temperature lower than 50°C . it usually forms calcite. Meigen assumes that the necessary cause of the formation of aragonite is decidedly a high temperature, but his assumption is not always correct. If CaCO_3 is deposited in an alkaline system, the precipitate becomes aragonite even at a low temperature, while in presence of free carbonic acid or in an acidic system, calcite is always deposited.

(1) W. Meigen, *Centralb. f. Min.*, 1901, 577.

This latter fact was first proposed by Warth,⁽¹⁾ and has been confirmed by the author. For instance, if an insufficient quantity of CaCl_2 is added to Na_2CO_3 aq. to precipitate CaCO_3 in alkaline system at an ordinary temperature, we obtain aragonitic substance, while on the other hand if a sufficient quantity of CaCl_2 is added to NaHCO_3 aq. with the constant evolution of CO_2 , we obtain calcite, when tested by Meigen's reactions.

Both of these precipitates consist of small crystals with an appearance of rhombohedron, although they are different in Meigen's reactions. One of them which is aragonitic in the reaction, is changed into calcite on the lapse of a few days, or sometimes even a few hours. In this case, Meigen denies the above proposal of Warth, and insists that such a substance with an aragonitic property is not really aragonite, but it is another substance such as *vaterite* for instance.

In fact, this unstable product gives the same reaction as aragonite, but is easily changeable to calcite.

On testing CaCO_3 secreted from the several kinds of Mollusca and lime algae by Meigen's method, the author found that most of these products consist of aragonite and ascertained their crystalline structure under microscope. The author has also collected the shells of Mollusca which have been allowed to stand 40 or 50 years, and has proved that they have been preserved as aragonite.

By these facts, it is clear that a high temperature is not necessary to obtain aragonite, in contradiction to Meigen's hypothesis.

The presence of slimy or gelatinous substance in the shells of Mollusca is also a noticeable fact, and the author comes to consider that this cementing substance is highly related to the formation of aragonite.

On the author's experiments, 1%-2% solution of gelatin is mixed with unstable aragonitic precipitate freshly prepared in a cold alkaline system, and is allowed to stand for a few months, in order to examine wheather the transformation of the above named precipitate into calcite is usual or not. After one, two or more months, the precipitate reacts aragonitic, i. e. its reaction is constant. The material treated as above is almost the same in appearance as the substance first taken, but is different in its stability, because the substance is no more unstable but exactly the same as ordinary aragonite.

Thus it is possible to obtain ordinary aragonite by precipitation at a low temperature in presence of gelatin. Generally, a gelatin solution is known as a protective colloid, and it seems to favour the formation of real aragonite.

(1) H. Warth, *Centralb. f. Min.*, 1902, 492.

Calcite is more stable than aragonite; therefore, the former is never changed into aragonite in the solution of gelatine. The author determined the value of P_H of both the solutions which had been prepared by boiling native aragonite and native calcite with distilled water. The result is as follows:—

Mineral.	P_H by electric method.	P_H by indicator method
Aragonite	8.2	8.4
Calcite	7.6	8.0

This shows also that there predominates the unstability or solubility of aragonite, because its hydrolysis depends upon the greater solubility.

Further the reactions of Meigen exactly coincide to the above results, i. e. on boiling the powder of aragonite with a dilute solution of $\text{Co}(\text{NO}_3)_2$, the powder is coloured violet, a basic cobalt carbonate being formed, while calcite is coloured sky-blue on long boiling with the same reagent, probably anhydrous cobalt carbonate being formed.

Furthermore, the aragonite powder suspended in water is coloured green by the addition of green vitriol, a basic ferrous sulphate being formed, while calcite on the same treatment is coloured yellow, at first probably the acidic solution of FeSO_4 being neutralized, and then ferric oxy-sulphate being formed by the oxydizing action of atmospheric oxygen.

It is probable that when carbonates are mixed with the solution of magnesium salts, magnesium carbonate is more or less produced, and the latter, which hydrolyses on dissolving in water, presents a noticeable alkaline reaction in the solution.

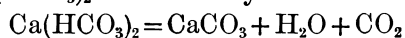
For the above reason, an effervescent spring and also sea water containing some magnesium salts have slight alkaline reactions, and have naturally a tendency of forming aragonite when CaCO_3 is precipitated in them.

Lastly, aragonite produced in hot springs frequently has a granular or oolitic form. Probably this is caused by the following functions:—

(1) The nucleus of the granule is deposited first with the evolution of CO_2 gas.

(2) Edges or tops of crystals are mostly dissolved by carbonic acid or are ground by mechanical revolution in water current.

Thus the precipitate becomes spherical and grows gradually through the decomposition of $\text{Ca}(\text{HCO}_3)_2$ as shown by the following equation:—



This conclusion is reached by the zonal structure of spherical grobules as well as by the etch figures on their surfaces with the consideration that they are formed by a dissolving action of carbonic acid.

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ON ENANTIOTROPY AND MONOTROPY. I.

By Noboru NAGASAKO.

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It can be considered that any polymorphism, including the cases where the number of modifications exceeds two, is composed of pairs of dimorphisms. The behaviours of dimorphism, therefore, play the fundamental rôle in the study of polymorphism. O. Lehmann⁽¹⁾ was the first in classifying dimorphism into two distinct categories, enantiotropy and monotropy. He stated: "Die charakteristische Eigentümlichkeit enantiotroper Modifikationen besteht in der Umkehrbarkeit des Umwandlungsvorganges bei der *normalen* Umwandlungstemperatur. . . . Ganz wesentlich verschieden hiervon verhalten sich die monotropen Modifikationen. . . . , denn die Umwandlung ist nicht umkehrbar, irreversibel. Bei dieser Klasse von Körpern existiert also eine im festen Zustande stets stabile und eine stets labile Modifikation, von welchen sich unter allen Umständen nur die letztere in die erstere umwandelt und zwar unter Freiwerden von Wärme." Later some interpretations on this subject were made by Ostwald, Schaum, Roozeboom, Tammann and others, on the basis of the phase theory.⁽²⁾ The definitions of the terms, enantiotropy and monotropy, however, have not been made which are consistent with the experimental cases. On this point, much ambiguities and incompleteness were found by the author. One of the chief objects of this paper is to make clear the definitions for them as well as the thermodynamic relations connected to them.

Definitions of Enantiotropy and Monotropy. The fundamental idea of O. Lehmann is to classify the behaviours of dimorphism, "under the atmospheric pressure" or "at the *normal* pressure", into two categories, enantiotropy and monotropy. We may, however, extend it more generally for the cases "at constant pressure." Some dimorphism which is enantiotropic or monotropic at one atmospheric pressure may change into the other by the effect of pressure.⁽³⁾ It is, therefore, necessary to add the condition of pressure or the range of pressure when we express in such cases, the relations of stability in terms of enantiotropy and monotropy.

(1) O. Lehmann, "Molekularphysik" (1888), I, p. 193.

(2) Wilh. Ostwald, *Z. physik. Chem.*, **22** (1897), 313; Schaum, *Lieb. Ann.* **300** (1897), 215; H.W.B. Roozeboom, "Die heterogenen Gleichgewichte" (1901), I, pp. 109, 159; G. Tammann, "Kristallisieren und Schmelzen" (1903), p. 101.

(3) O. Lehmann gave no remarks on the effects of pressure on the stability of dimorphism as is clear in the quotation given above.

Let us now interpret more closely the term, "transition." Two types of transition are probable. One is the case in which it occurs from the metastable to the stable⁽¹⁾ modification, the other is the case in which it occurs from the metastable to the metastable modification. In general, the first case occurs in nature. And as the experimental fact, fairly smooth phase changes occur from the solid to the liquid or the gaseous phase. Hence, in the use of the terms enantiotropy and monotropy, it will be convenient to confine it only in such cases, in which the transition occurs from the metastable to the stable modification and the phase changes from the two modifications to any other phases are free from the effects of pseudoequilibrium.

We may now define enantiotropy by the following two conditions at constant pressure:

- (1) There should be (neutral) equilibrium temperature between the two modifications A and B in one component.⁽²⁾
- (2) In the neighbourhood thereof, A should be stable above it, B being stable below it, or vice versa.

The dimorphism which does not satisfy the above conditions at constant pressure is defined to be monotropy, if only one of the two modifications is stable. With the above conditions in mind, we are able to consider that monotropy is included in the following cases:

- (i) The dimorphism without any equilibrium temperature.⁽³⁾
- (ii) The dimorphism with equilibrium temperature only in the unstable domain of A and B.
- (iii) The dimorphism with equilibrium temperature, however, only A (or B) is stable except there.

By means of a few examples these definitions will be more clear. The schematically drawn pT -diagrams⁽⁴⁾ of sulphur, methylene iodide and phenol are shown in Fig. 1, Fig. 2 and Fig. 3 respectively. Fig. 1 is the case in which the enantiotropic dimorphism at one atmospheric pressure changes into the monotropic at high pressure. Fig. 2 is the case in which the monotropic dimorphism at low pressure changes into the enantiotropic at high pressure. In Fig. 3 we found one of the examples with two transition points at constant pressure.

- (1) The term "stable" will be used in the sense of "more stable than any other phases."
- (2) When clear, the condition of "one component" will be omitted. And the two modifications will be considered to satisfy the condition of "pure homogeneous phase".
- (3) After the general customs of the study in this field, equilibrium temperature is considered even in the unstable domain. Monotropy (i) is the case in which such temperature cannot be considered both in the stable and unstable domains of the two modifications.
- (4) G. Tammann, loc. cit. p. 270 (sulphur); p. 280 (methylene iodide); p. 310 (phenol). As for methylene iodide, cf., A.H.R. Müller, *Z. physik. Chem.*, **86** (1913), 237.

In our definitions, it is enantiotropic at P_2 in Fig. 1 and at P_3 in Fig. 2. At P_1 and P_2 in Fig. 3 we have the enantiotropy with two transition points. At P_1 one of the transition points lies in the unstable domain, the rest being in the stable domain. It may be mentioned here that it cannot always be monotropic even if one of the transition points lies in the unstable domain. At P_4 in Fig. 3 we have one of the examples for monotropy (i), and at P_3 in Fig. 1 and at P_2 in Fig. 2, monotropy (ii), and also at P_3 in Fig. 3, monotropy (iii). It is evident that we have always monotropy (iii) and (ii), at and below the pressure of the triple point among two solids and gas, as at P_1 in Fig. 1 and Fig. 2. And also we have monotropy (iii) at the pressure of the triple point among two solids and liquid in Fig. 1 and Fig. 2.

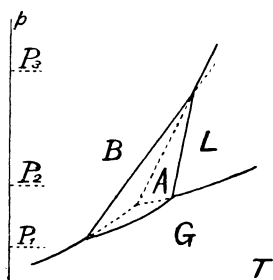


Fig. 1.

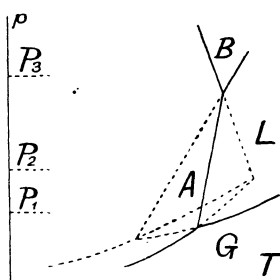


Fig. 2.

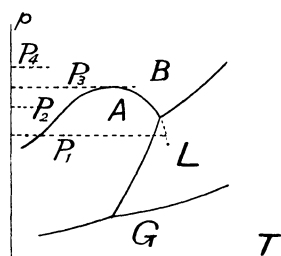


Fig. 3.

Criteria of Mutual Stability and Equilibrium. In the pT -diagram, the most convenient criteria for equilibrium and stability is the Gibbs' ζ -function. In order to know the mutual stability of the two modifications A and B at the point (pT) , we have to consider the difference Z of the specific values of ζ -function for A and B.

$$Z = \zeta_B - \zeta_A, \quad \text{or} \quad Z = X - Q,$$

where X is the heat absorbed when the transition occurs naturally from A to B at constant temperature and pressure, or the calorimetric heat of transition; and Q is the heat absorbed when it is made in the reversible way at constant temperature.

A and B are in equilibrium when $Z=0$, or $X=Q$. It is clear that A is more stable than B when $Z>0$, or $X>Q$, for such a change cannot occur in nature in which the calorimetric heat is greater than that of the reversible change as before. And also B is more stable than A when $Z<0$, or $X<Q$.

At constant pressure, we have $Z=f(T)$, or Z varies only with the variation of temperature along the curve $f(T)$. If we let the equilibrium temperatures be $T_0, T_0', \dots$ etc., we have these as the roots of the equation $f(T)=0$, or $Z=0$. It is, therefore, necessary to investigate the nature of the equation $f(T)=0$, or the nature of the Z -curve, in order to find the equilibrium

point as well as to know the relation of mutual stability in the given dimorphism at constant pressure.

We have monotropy (i) if there is no real root in the equation $Z=0$, and only one modification is stable. If there is one real and positive root T_0 in the equation $Z=0$, the behaviour of the Z -curve will be as in Fig. 4.

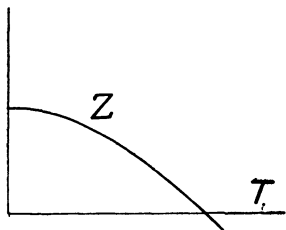


Fig. 4.

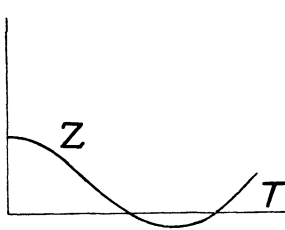


Fig. 5.

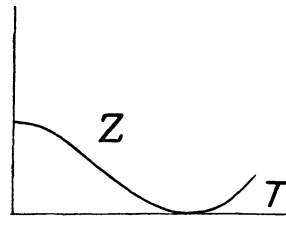


Fig. 6.

If there is only one melting point for each modification at constant pressure, we shall have monotropy (ii) when T_0 lies above the melting point; and also enantiotropy, when below. We shall next consider the cases with two real and positive roots in the equation $Z=0$, each modification having only one melting point. In these cases, we shall have in general enantiotropy or monotropy (ii) as before. The behaviour of the Z -curve is as in Fig. 5. However, if the two roots are equal, the Z -curve will be brought in contact with the T -axis as in Fig. 6, which is the case at P_3 in Fig. 3. In this case, the two modifications have an equilibrium point. However, if the transition is made to occur directly⁽¹⁾ at the pressure under considerations, it shall be limited in one direction as in monotropy (i) and (ii). It is not enantiotropic and may be ascribed to monotropy (iii).⁽²⁾

We may therefore consider enantiotropy,⁽²⁾ on the basis of thermodynamics, as follows; It shall be enantiotropic when Z -curve cuts T -axis between the stable domain of the two modifications. In which case, the direct transition shall occur in two opposite directions above and below the transition point.

Besides above cases, we may be able to consider lots of special cases and the cases in which two melting points exist for each modification at constant pressure. However, these cases are omitted here, for the sake of brevity and owing to the lack of the experimental examples.

Some Theories hitherto Proposed on Enantiotropy and Monotropy and the Cases of Pseudequilibriums. It was first proposed by Ostwald⁽³⁾ that

- (1) We have to add the condition, "directly", or "without any intermediate states including ion." For instance, the red phosphorus changes into the white when heated and distilled. Whereas these modifications stand in the relation of monotropy under the atmospheric pressure.
- (2) Monotropy (Gr. *monos*—single; *tropos, trepein*—to change) and enantiotropy (Gr. *enantios*—opposite; *tropos, trepein*—to change).
- (3) Wilh. Ostwald, loc. cit.

it is enantiotropic or monotropic according as the transition point lies below or above the melting point. It is implied in this statement that, under the atmospheric pressure, there is only one melting point for each modification, and one transition point between the two modifications, which is an experimental rule adopted by many authors. Our monotropy (i) and (iii) were not included here. The category of pseudomonotropy was proposed by Roozeboom,⁽¹⁾ in order to make more complete the Ostwald's theory on monotropy, in which following cases were included :

- (a) The dimorphism with its transition point in the low temperature where the transition is retarded. In which cases, it may manifest itself like monotropic.
- (b) The dimorphism with the equilibrium point at absolute zero.

In the foregoing paragraphs, such cases have been excluded in which the phase changes from the two modifications to any other phases are disturbed by the effects of pseudequilibrium. It is, however, probable that there are the cases in which the dimorphism appears like enantiotropic by such effects which may be called pseudenantiotropy. It is also probable that there are the cases which appear like monotropic and yet can not be classified in our monotropy. It may be called pseudomonotropy. In which the case of (a) in the pseudomonotropy of Roozeboom may be included although it is not necessary to distinguish it from enantiotropy from the thermodynamic standpoint. The case of (b) is nothing but the special case of our monotropy (iii). It may be added here that in the cases of pseudenantiotropy and pseudomonotropy the effects of pseudequilibrium or retardation are necessary.

In a later paper, it will be discussed how our Z -function varies with the temperature and pressure in conjunction with the measurable quantities, and some ambiguous or abstruse cases will be treated.

In conclusion, I would express my hearty thanks to Prof. J. Sameshima whose counsels have been constantly at my disposal.

Summary.

It is a well known fact that there are two distinct behaviours of dimorphism in which transitions are of reversible and irreversible natures. O. Lehmann was the first in classifying it by the two categories, enantiotropy and monotropy. Later it was interpreted by Ostwald and others on the basis of the phase theory. However, clear definitions have not been made so far, which are consistent with all the experimental cases in the wide range of pT -diagram. To make it more complete and concrete, some definitions are

(1) H.W.B. Roozeboom, loc. cit., p. 177.

given for the terms enantiotropy and monotropy. These terms not only serve to express the absolute stability but also to express the mutual stability of the two modifications in one component. The thermodynamic relations connected to them are also described. The cases of pseudoequilibrium are also spoken of. As the result of these considerations, various theories on enantiotropy and monotropy are brought into one conformity.

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ON THE OXIDATION OF THE MIXTURE OF STANNOUS
HYDROXIDE AND SODIUM SULPHITE IN SODIUM
CARBONATE SOLUTION WITH AIR.

By Susumu MIYAMOTO.

Received February 28, 1928. Published April 28, 1928.

Introduction. It was observed that the mixture of sodium sulphite and stannous hydroxide in sodium hydroxide solution oxidizes very slowly first with air, when the initial concentration of stannous hydroxide is small.⁽¹⁾ The author has an opinion to explain the fact by the transference of active states.⁽²⁾ If we accept the idea that the active states of the molecules of sodium sulphite transfers to the molecules of stannous hydroxide, it is easy to explain the experimental results as follows.

When the concentration of stannous hydroxide is very small, the oxidation velocity of the mixture with air should be very small first, for stannous hydroxide oxidizes alone, if the active states of the molecules of sodium sulphite transfer to the molecules of stannous hydroxide. After the disappearance of the molecules of stannous hydroxide by the oxidation, sodium sulphite begins to oxidize and the oxidation velocity of the mixture increases. Thus the oxidation of the mixture in sodium hydroxide solution, which will be regarded as a kind of negative induced reaction, can be explained by the transference of active states.

According to this idea, the mixture of sodium sulphite and stannous hydroxide in sodium carbonate solution, should oxidize very slowly, for the oxidation velocity of stannous hydroxide in sodium carbonate solution⁽³⁾ is very small, though sodium sulphite oxidizes quickly, if it be alone.⁽⁴⁾ The present research was carried out to ascertain this idea.

(1) S. Miyamoto, this journal, 2 (1927), 196.

(2) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, 4 (1926), 259

(3) S. Miyamoto, this journal, 3 (1928), 43.

(4) S. Miyamoto, *ibid.*, 3 (1928), 76.

Experimental: The experimental procedure was quite the same as that employed in the previous study on the oxidation of the mixture in sodium hydroxide solution.⁽¹⁾ In the following Tables, v is the volume of sodium thiosulphate solution of 0.0996 normal which is equivalent to the total amount of sodium sulphite and stannous chloride, $v_0(\text{SnCl}_2)$ and $v_0(\text{Na}_2\text{SO}_3)$ being the initial amounts of stannous chloride and sodium sulphite respectively.

If the oxidation of stannous hydroxide take place alone, v should have the value v' given in the following tables, which was calculated by $v' = v_0 - k't$, k' being the velocity constant of the oxidation of stannous hydroxide in sodium carbonate solution given in the previous paper.

If sodium sulphite oxidize alone, v should have the value v'' given in the following tables, which was calculated by $v'' = v_0 - k''t$, k'' being the velocity constant of the oxidation of sodium sulphite and calculated by $k = 0.258 - 0.114 C_{\text{Na}_2\text{CO}_3}$, given in the previous paper.

TABLE 1.

Temp.=20°C. $C_{\text{Na}_2\text{CO}_3}=0.2780$ normal.

Velocity of air=7.78 litres per hour.

$v_0(\text{SnCl}_2)$ c.c.	$v_0(\text{Na}_2\text{SO}_3)$ c.c.	t min.	v c.c.	v' c.c.	v'' c.c.
12.98	2.89	0	15.87	—	—
		15	15.73	15.77	—
		30	15.70	15.66	—
		60	15.62	15.46	—
8.14	11.32	0	19.46	—	—
		10	19.30	19.39	17.20
		30	19.19	19.25	12.68
		60	19.05	19.05	5.90
1.69	19.82	0	21.51	—	—
		10	21.39	21.44	19.25
		40	21.09	21.23	12.47
		60	21.03	21.10	7.95
0.42	13.72	0	14.14	—	—
		10	13.95	—	11.88
		30	13.75	—	7.36
		60	13.47	—	0.58
0.13	20.48	0	20.61	—	—
		10	20.06	—	18.35
		50	20.03	—	9.31
0.031	15.33	0	15.36	—	—
		10	15.20	—	13.10
		30	10.95	—	8.57
		60	5.46	—	1.80

(1) Loc. cit.

TABLE 2.

Temp. = 20°C. $C_{\text{Na}_2\text{CO}_3} = 0.4655$ normal.

Velocity of air = 7.78 litres per hour.

$v_0(\text{SnCl}_2)$ c.c.	$v_0(\text{Na}_2\text{SO}_3)$ c.c.	t min.	v c.c.	v' c.c.	v'' c.c.
16.74	1.21	0	17.95	—	—
		10	17.90	17.88	—
		30	17.80	17.74	—
		60	17.68	17.54	—
7.93	10.71	0	18.64	—	—
		10	18.56	18.57	16.59
		30	18.40	18.43	12.49
		60	18.29	18.23	6.34
1.66	13.71	0	15.37	—	—
		15	15.19	15.27	12.29
		35	14.99	15.13	8.19
		60	14.85	14.96	3.07
0.44	18.25	0	18.69	—	—
		10	18.48	—	16.64
		60	18.20	—	6.39
0.12	16.37	0	16.49	—	—
		10	16.17	—	14.44
		30	15.85	—	10.34
		60	15.78	—	4.19
0.024	16.22	0	16.24	—	—
		8	16.15	—	14.60
		25	12.75	—	11.11
		50	8.29	—	5.99

It seems from Table 1 and 2, that stannous hydroxide alone is oxidized, when air is passed into the mixture in sodium carbonate solution, as is expected. When the initial concentration of stannous hydroxide is very small, the mixture is oxidized very slowly first and increases afterwards, as is shown in the Tables. The result is easily explained quite the same way as in the case of the oxidation of the mixture in sodium hydroxide solution, by accepting the idea above described.

Thus the oxidation of the mixture of stannous hydroxide and sodium sulphite is an example of negative induced reaction; the oxidation of the first substance has an inhibiting action on the oxidation of the second one. The mechanism of the reaction can be explained by the transference of active states.⁽¹⁾

Summary.

1. The oxidation of the mixture of sodium sulphite and stannous hydroxide in sodium carbonate solution was studied.

(1) Loc. cit.

2. It was observed that the reaction is an example of negative induced reaction; the oxidation of stannous hydroxide has an inhibiting action on the oxidation of sodium sulphite.

3. The mechanism of the reaction was discussed.

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO SODIUM HYDROXIDE, SODIUM CARBONATE AND HYDROCHLORIC ACID SOLUTION.

By Susumu MIYAMOTO.

Received March 3, 1928. Published April 28, 1928.

Studies on the oxidation velocities by means of air of several substances, such as ferrous hydroxide,⁽¹⁾ sodium sulphite,⁽²⁾ stannous hydroxide,⁽³⁾ and the mixture of sodium sulphite and stannous hydroxide⁽⁴⁾ in sodium hydroxide solution, stannous chloride in hydrochloric acid solution,⁽⁵⁾ stannous hydroxide,⁽⁶⁾ sodium sulphite,⁽⁷⁾ and the mixture of sodium sulphite and stannous hydroxide⁽⁸⁾ in sodium carbonate solution, were carried out.

This kind of heterogeneous reactions can be considered to take place in three stages, firstly, a part of the molecules of oxygen, which strike the surface of air bubbles, enters into the liquid surface film, secondly, the oxidation occurs in the liquid phase (principally in the surface film), thirdly, the reacting substances in the inner liquid phase diffuse to the surface of the bubbles, and the oxygen dissolved in the surface film diffuses into the inner liquid phase. The slowest process will determine the velocities of these heterogeneous reactions. If the second or the third process be the slowest, the oxidation velocity should depend on the concentrations of the reacting substances. If sufficient reacting substances be always present to react with oxygen as soon as it enters in the surface film, that is, if the concentration of oxygen in the surface film be always kept zero, the apparent oxidation

(1) This journal, 2 (1927), 40.

(2) Ibid., 2 (1927), 74.

(3) Ibid., 2 (1927), 155.

(4) Ibid., 2 (1927), 191.

(5) Ibid., 2 (1927), 259.

(6) Ibid., 3 (1928), 43.

(7) Ibid., 3 (1928), 76.

(8) Ibid., 3 (1928), 95.

velocity is no other than the rate of the first process, the dissolution of oxygen, and will be independent of the concentration of the reacting substances, if the partial pressure of oxygen be kept constant.

Under these conditions, the meaning of the dissolution velocity of oxygen is quite different from that of the dissolution velocity of solid substances in the liquid phase, in which case the process of diffusion governs the velocity. The oxidation velocities of the substances above described with air were almost in every case independent of the concentrations of the reacting substances under the conditions of the author's measurements, if the initial concentrations of the reacting substances be not very small. In these cases, the observed apparent oxidation velocities do not mean the true oxidation velocities of the substances, but the dissolution velocity of oxygen, the meaning of which being above described, into the liquid phase. It is then possible to calculate the approximate values of the dissolution velocity of oxygen into sodium hydroxide, sodium carbonate and hydrochloric acid solution, when air was passed into 40 c.c. of the solution in a test tube (diameter $\doteq$ 3 cm.) through a glass tube (inside diameter $\doteq$ 4 mm., outside diameter $\doteq$ 6 mm.) at the rate of 7.78 litres per hour, from the results of the author's studies. The calculated values are given in Table 1. The concentrations are given in the first column and the dissolution velocities in the second, the third, and the fourth column, some of them being already given in the previous papers.

The results are also shown graphically in Fig. 1.

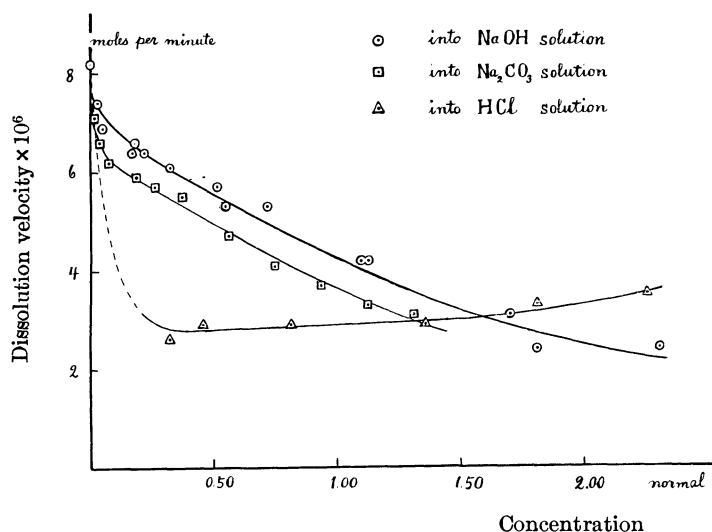


Fig. 1.

TABLE 1.

Temp. = 20°C.

Concentrations normal	Dissolution Velocity of Oxygen $\times 10^6$ moles per min.		
	in NaOH	in Na ₂ CO ₃	in HCl
0	8.2 ⁽¹⁾	8.2 ⁽¹⁾	8.2 ⁽¹⁾
0.01875	—	7.1 ⁽¹⁾	—
0.02888	7.4 ⁽¹⁾	—	—
0.03750	—	6.6 ⁽¹⁾	—
0.05173	6.9 ⁽¹⁾	—	—
0.0750	—	6.2 ⁽¹⁾	—
0.1706	6.4 ⁽²⁾	—	—
0.1810	6.6 ⁽¹⁾	—	—
0.1875	—	5.9 ⁽¹⁾	—
0.2204	6.4 ⁽²⁾	—	—
0.2625	—	5.7 ⁽¹⁾	—
0.3235	—	—	2.6 ⁽³⁾
0.3252	6.1 ⁽²⁾	—	—
0.3750	—	5.5 ⁽¹⁾	—
0.4587	—	—	2.9 ⁽³⁾
0.5173	5.7 ⁽¹⁾	—	—
0.5500	5.3 ⁽²⁾	—	—
0.5630	—	4.7 ⁽¹⁾	—
0.7219	5.3 ⁽¹⁾	—	—
0.750	—	4.1 ⁽¹⁾	—
0.8151	—	—	2.9 ⁽³⁾
0.938	—	3.7 ⁽¹⁾	—
1.1011	4.2 ⁽¹⁾	—	—
1.125	—	3.3 ⁽¹⁾	—
1.130	4.2 ⁽²⁾	—	—
1.313	—	3.1 ⁽¹⁾	—
1.360	—	—	2.9 ⁽³⁾
1.704	3.1 ⁽²⁾	—	—
1.810	2.4 ⁽¹⁾	—	—
1.811	—	—	3.3 ⁽³⁾
2.262	—	—	3.5 ⁽³⁾
2.312	2.4 ⁽²⁾	—	—

(1) The values calculated from the oxidation velocity of sodium sulphite.

(2) " " " " " stannous hydroxide.

(3) " " " " " stannous chloride.

Ferrous hydroxide in sodium hydroxide solution and stannous hydroxide in sodium carbonate solution exist as solid phase in the system and the mechanism of the oxidation of them will be more complex, and the experimental results are not sufficient to discuss it precisely, but from the experimental results, the apparent oxidation velocity of the former seems to be the dissolution velocity of oxygen and that of the latter the reacting velocity.

The author has an opinion to explain some catalysis and induced reaction by the transference of active states.⁽¹⁾ It was ascertained that the increase of the velocity of the induced oxidation of some carbohydrates in the presence of ferrous hydroxide or sodium sulphite with the increase of

(1) *Scientific Papers of the Institute of Physical and Chemical Research*, 4 (1926), 257.

the concentration of sodium hydroxide, studied by C.C. Palit and N.R. Dhar,⁽¹⁾ is not due to the increase of the velocity of the primary reaction; the oxidation velocity of ferrous hydroxide⁽²⁾ or sodium sulphite⁽³⁾ decreases with the increase of the concentration of sodium hydroxide. The phenomenon can easily be explained by the transference of the active states of the molecules of the products or the reacting substances of the primary reaction to the molecules of the reacting substances of the secondary reaction.

As was discussed already in the previous papers, the oxidation of the mixture of stannous hydroxide and sodium sulphite can be regarded as a kind of negative induced reactions; the oxidation velocity of sodium sulphite is extremely small in the presence of stannous hydroxide.

According to the author's opinion, some negative induced reactions are explained by the transference of the active states of the molecules of the reacting substances of the secondary reaction to the molecules of some reacting substances or reaction products of the primary reaction, and the oxidation velocity of the mixture studied can be explained by the transference of the active states of the molecules of sodium sulphite to the molecules of stannous hydroxide. The transference of the active states of the molecules of sodium sulphite to the molecules of other substances seems to occur easily, which will be the cause of the existence of many negative catalysers⁽⁴⁾ on the oxidation of sodium sulphite.

The catalytic effect of inert gases on some reactions under the influence of alpha-particles, studied by S. C. Lind and D. C. Bardwell,⁽⁵⁾ is an experimental result favourable to the author's theory. The phenomenon can be explained as the result of the transference of active states of the molecules of inert gases, excited by alpha-particles, to the molecules of the reacting substances.

Summary.

1. The dissolution velocity of oxygen when air was passed into sodium hydroxide, sodium carbonate and hydrochloric acid solution under some conditions was calculated from the oxidation velocities of sodium sulphite, stannous hydroxide and stannous chloride.

2. The mechanism of some negative induced reactions was discussed.

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Hongo, Tokyo.

(1) *J. Phys. Chem.*, **29** (1925), 799; **30** (1926), 939

(2) Loc. cit.

(3) Loc. cit.

(4) S. L. Bigelow, *Z. physik. Chem.*, **26** (1898), 493; A. Titoff, *Z. physik. Chem.*, **45** (1903), 641; S.W. Young, *J. Am. Chem. Soc.*, **24** (1902), 297.

(5) *J. Am. Chem. Soc.*, **48** (1926), 1575.

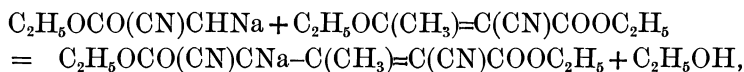
SYNTHESIS OF DIETHYL β -METHYL- α , γ -DICYANOGLUTACONATE.

By Yoshiyuki URUSHIBARA.

Received February 27, 1928. Published April 28, 1928.

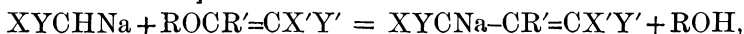
Diethyl β -methyl- α , γ -dicyanoglutaconate could not be obtained by the reaction of ethyl sodio-cyanoacetate and ethyl α -cyanoacetoacetate.⁽¹⁾ The formation of the same substance can not be expected in the reaction of methylchloroform with ethyl cyanoacetate in the presence of sodium ethylate, for it is known that methylchloroform does not react with diethyl malonate in the presence of sodium ethylate.

The condensation of ethyl ethoxy-ethylidene-cyanoacetate (ethyl β -ethoxy- α -cyanocrotonate) $\text{CH}_3\cdot\text{C}(\text{OC}_2\text{H}_5)=\text{C}(\text{CN})\text{COOC}_2\text{H}_5$ with ethyl sodio-cyanoacetate has been tried with success. In this reaction diethyl α -sodio- β -methyl- α , γ -dicyanoglutaconate is produced according to the following equation :



and from it diethyl β -methyl- α , γ -dicyanoglutaconate $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{CH}-\text{C}(\text{CH}_3)=\text{C}(\text{CN})\text{COOC}_2\text{H}_5$ is obtained by the action of dilute hydrochloric acid.

In a previous paper⁽²⁾ the author described the synthesis of the nitrile-esters of dicarboxyglutaconic acid by similar condensations, in which ethoxy-methylene compounds were used instead of the ethoxy-ethylidene compound. Thus it has been ascertained that the reaction represented by the following general equation can take place :



where R represents any alkyl group, R' hydrogen or any alkyl group, and X, X', Y, Y' negative groups such as CN or COOC_2H_5 . It seems possible that the other nitrile-esters of β -methyldicarboxyglutaconic acid will be synthesized by the similar method.

In a previous paper⁽³⁾ it was shown that the diethyl α -sodio- α , γ -dicyanoglutaconate $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{CH}-\text{CNa}(\text{CN})\text{COOC}_2\text{H}_5$ does not yield the corresponding free nitrile-ester on acidifying its aqueous solution, but a semihydrate with the formula $(\text{C}_{10}\text{H}_{12}\text{O}_4\text{N})-\text{C}(=\text{NH})-\text{NH}-\text{CO}-(\text{C}_{10}\text{H}_{12}\text{O}_4\text{N})$ is precipitated as yellow crystals. G. Errera and F. Perciabosco⁽⁴⁾ showed that the sodium derivative of triethyl dicyanoaconitate $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C}=\text{C}(\text{COOC}_2\text{H}_5)-$

(1) This journal, 2 (1927), 305.

(2) This journal, 2 (1927), 278.

(3) This journal 2 (1927), 28.

(4) *Ber.*, 34 (1901), 3704.

$\text{CNa}(\text{CN})\text{COOC}_2\text{H}_5$ is transformed into a semihydrate on acidifying its aqueous solution. But the hydration does not take place in the β -methyl compound, i. e. diethyl β -methyl- α , γ -dicyanoglutaconate, as described above.

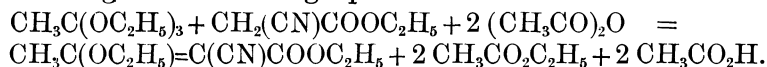
The compound, represented by the formula $\text{C}_2\text{H}_5\text{OC}(\text{CH}_3)=\text{C}(\text{CN})\text{COOC}_2\text{H}_5$ and designated with the name of ethyl ethoxy-ethylidene-cyanoacetate, is already known as ethyl β -ethoxy- α -cyanocrotonate and synthesized by the action of ethyl iodide on the silver derivative of ethyl α -cyano-acetoacetate.⁽¹⁾ The author has obtained the same substance by the condensation of triethyl orthoacetate with ethyl cyanoacetate by means of acetic anhydride, a reaction analogous to those in which ethoxy-methylene compounds are formed,⁽²⁾ and has ascertained that the ortho-ester can generally condense with methylene compounds such as ethyl cyanoacetate according to the following equation:

$$\text{R}'\text{C}(\text{OR})_3 + \text{CH}_2\text{XY} + 2(\text{CH}_3\text{CO})_2\text{O} = \text{ROCK}'=\text{CXY} + 2\text{CH}_3\text{CO}_2\text{R} + 2\text{CH}_3\text{CO}_2\text{H},$$

where R represents any alkyl group, R' hydrogen or any alkyl group, and X, Y negative groups such as CN or COOC_2H_5 .

Condensation of Triethyl Orthoacetate and Ethyl Cyanoacetate by means of Acetic Anhydride. — **Preparation of Ethyl Ethoxy-ethylidene-cyanoacetate.** The mixture of triethyl orthoacetate, ethyl cyanoacetate, and acetic anhydride in the proportion of 1 mol: 1 mol: 2mols is heated in a flask with a reflux condenser. The cooling water is stopped from running and a tube bent downwards is attached to the top of the condenser, so that the reflux condenser separates acetic anhydride from ethyl acetate formed during the reaction, when the cooling water is sufficiently warm, and the ethyl acetate is cooled to condense in the bent tube and can be collected. When ethyl acetate reaches the required quantity, and distils no more, the content of the flask is distilled at first under the ordinary pressure and then under diminished pressure. The portion distilling at 152.5° under the pressure of 7 mm. is collected. Otherwise the residue in the flask may be recrystallised from alcohol after acetic anhydride and unchanged esters have been driven off by vacuum distillation.

Ethyl ethoxy-ethylidene-cyanoacetate prepared by the above method is colourless crystals, contains 7.66% of nitrogen (the formula requires N = 7.65 %), and, when recrystallised from alcohol a few times, melts at $74-75^\circ$. This is the same as ethyl ethoxy-cyanocrotonate synthesized by Haller, and is formed according to the following equation:



(1) Haller, *Compt. rend.*, **130** (1900), 1223.

(2) *Ann.*, **297** (1897), 1; *Bull. soc. chim.*, [3], **25** (1901), 21.

Condensation of Ethyl Ethoxy-ethylidene-cyanoacetate with Ethyl Sodicyanoacetate.—**Synthesis of Diethyl β -Methyl- α, γ -dicyanoglutaconate.** Ethyl ethoxy-ethylidene-cyanoacetate prepared by the above method was added to the equivalent amount of ethyl sodio-cyanoacetate in absolute alcohol. The clear reddish yellow solution was allowed to crystallise at the room temperature. The crystalline substance was collected and recrystallised from absolute alcohol. 0.1875 Gr. of the substance gave 16.85 c. c. of nitrogen at 14°, 758.2 mm. (Found: N=10.50. $C_{12}H_{13}O_4N_2Na$ requires N=10.29%.) This compound is diethyl α -sodio- β -methyl- α, γ -dicyanoglutaconate and the condensation is represented by the equation indicated in page 103.

The sodium compound is nearly colourless and very easily soluble in water. The aqueous solution deposited an oily substance on acidifying with dilute hydrochloric acid. This oil was taken with ether, but when the ether was driven away from the solution, it did not remain colourless for a long time and changed into a red crystalline mass. For this reason it was impossible to ascertain the formula of this compound by analysis. (Found: C=56.57, 55.91; H=5.68, 5.62; N=11.05, 11.04. $C_{12}H_{14}O_4N_2$ requires C=57.58; H=5.64; N=11.20%.) That this substance is not a semihydrate is evident from the following facts: (I) It is precipitated immediately when the aqueous solution of the sodium derivative is acidified, and (II) it is soluble in ether.⁽¹⁾ This is diethyl β -methyl- α, γ -dicyanoglutaconate with the formula $C_2H_5OCO(CN)CH-C(CH_3)=C(CN)COOC_2H_5$.

A silver derivative was obtained in colourless fine crystals when equivalent amounts of the sodium compound and of silver nitrate were mixed in aqueous solutions. It was purified by recrystallisation from alcohol. 0.2953 Gr. of the silver compound gave 0.4319 gr. of CO_2 and 0.0927 gr. of H_2O ; 0.2806 gr. of the substance gave 0.4095 gr. of CO_2 and 0.0882 gr. of H_2O ; 0.3626 gr. of the substance gave 24.25 c. c. of nitrogen at 15°, 769.3 mm. (Found: C=39.90, 39.81; H=3.51, 3.52; N=7.89. $C_{12}H_{13}O_4N_2Ag$ requires C=40.34; H=3.67; N=7.84%.) These numbers show that the substance could not be perfectly purified by recrystallisation from alcohol.

Another specimen of diethyl sodio- β -methyl-dicyanoglutaconate was prepared by the condensation of ethyl sodiocyanoacetate with ethyl ethoxy-ethylidene-cyanoacetate (ethyl ethoxycyanocrotonate) synthesized from the silver derivative of ethyl cyanoacetoacetate and ethyl iodide, and it was converted into the silver derivative, which was recrystallised from alcohol. 0.2962 Gr. of the substance gave 0.4358 gr. of CO_2 and 0.0948 gr. of H_2O ; 0.3449 gr. of the substance gave 23.4 c. c. of nitrogen at 13°, 755.5 mm. (Found: C=40.14; H=3.58; N=7.85. $C_{12}H_{13}O_4N_2Ag$ requires

(1) Cf. this journal, 2 (1927), 29.

C=40.34 ; H=3.67 ; N=7.84%.) The latter specimen seems to be purer than the former, and it is probable that the impurity causing the deviation of the analytical result in the former came from the starting substance, i. e. ethyl ethoxyethylidene-cyanoacetate.

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART VI.⁽¹⁾

By Taku UEMURA and Shozo TABEL.

Received February 27, 1928. Published April 28, 1928.

One of the writers⁽²⁾ has already discussed on the tautomeric transformations of some hydroxyazo-compounds and assigned them different formulas which were derived from the results of alkaline reactions.

We have now to consider the position of the hydroxyl-group with regard to the azo-group, for in a previous report⁽³⁾ we came to the conclusion that the shape of the absorption bands is probably altered by the insertion of the methyl-group into a benzene nucleus.

But we intend to take another point of view owing to the position of the hydroxyl-group which is included in these compounds. Though our last two papers described this assumption, we shall here again confirm this observation.

Experimental. m-Acetylamino-o-hydroxyazobenzene⁽⁴⁾ clearly represents two bands in its absorption curve (Fig. 1). The auxochromic power of the amino-group is nearly lost by acetylation and this is easily understood in comparing the absorption curves of azobenzene ($\langle \text{C}_6\text{H}_5 \rangle\text{--N:N--}\langle \text{C}_6\text{H}_5 \rangle$), p-acetylaminoazobenzene⁽⁵⁾ ($\langle \text{C}_6\text{H}_4 \rangle\text{--N:N--}\langle \text{C}_6\text{H}_4 \rangle\text{--NHCOCH}_3$) and

(1) Read before the Chemical Society of Japan, February 18, 1928.

(2) Uemura, Yokojima and Tan, this journal, **1** (1926), 260; Uemura, Yokojima and Endo, *ibid.*, **2** (1927), 10 & 48; Uemura and Tabei, *ibid.*, **2** (1927), 229 & 249.

(3) This journal, **2** (1927), 51.

(4) Hewitt and Ratcliffe, *J. Chem. Soc.*, **101** (1912), 1765.

(5) Berju, *Ber.*, **17** (1884), 1400.

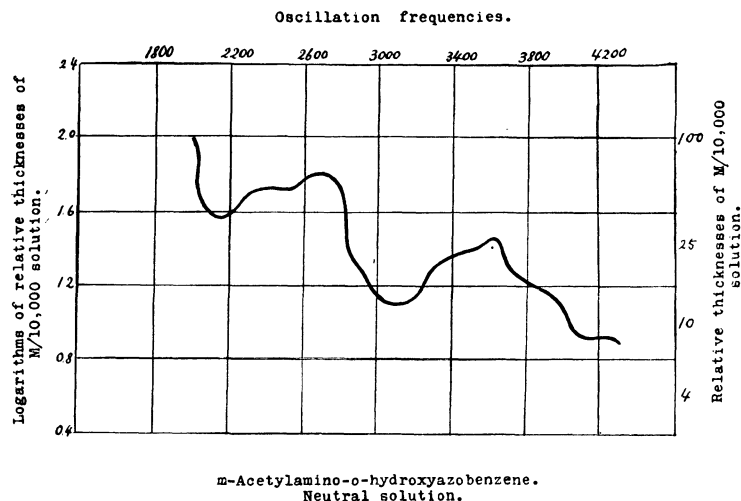


Fig. 1.

p-aminoazobenzene($\text{C}_6\text{H}_5\text{--N=N--C}_6\text{H}_5$) (Fig. 2). The absorption curve of *p*-acetylaminazobenzene approaches to that of azobenzene in the alcoholic solution, while on the contrary *p*-aminoazobenzene shows the considerable bathochromic influence in its curve. This proves that the auxochromic effect of the amino-group is remarkably weakened when acetylated.

Hence we may conclude that the absorption curve given by the neutral solution of *m*-acetyl-amino-*o*-hydroxyazobenzene is not caused by the acetyl-amino-group but by the hydroxyl-group. So far as our studies are concerned, *o*-hydroxyl with respect to the azo-group has always two absorption bands.

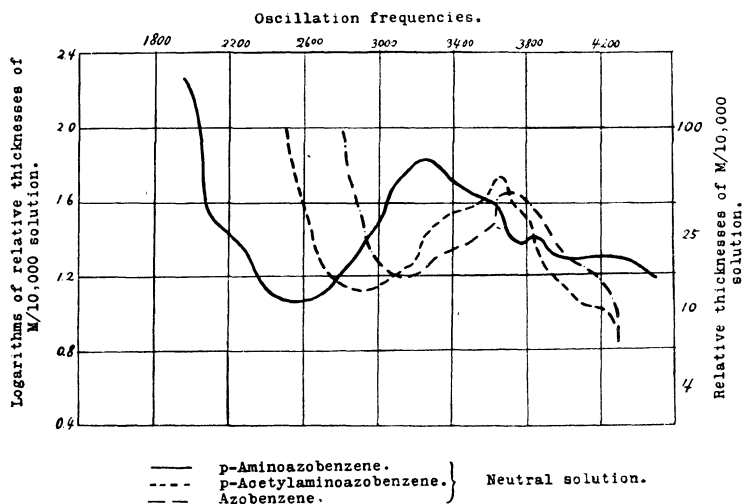


Fig. 2.

The following hydroxyazo-compounds, which appeared in previous papers, have two absorption bands on account of the o-hydroxyl-group with respect to the azo-group.

Benzeneazo-p-cresol.⁽¹⁾

p-Nitrobenzeneazo-p-cresol.⁽¹⁾

o-Tolueneazo-p-cresol.⁽²⁾

m-Tolueneazo-p-cresol.⁽²⁾

p-Tolueneazo-p-cresol.⁽²⁾

o-Nitrobenzeneazo-p-cresol.⁽³⁾

m-Nitrobenzeneazo-p-cresol.⁽³⁾

Summary.

1. The o-hydroxyl-group in hydroxyazo-compounds gives rise to two bands in their absorption curves.

2. The methyl-group shows perhaps no influence upon the shape of the absorption curves of hydroxyazo-compounds.

We wish to express our sincere thanks to Prof. Yuji Shibata of the Tokyo Imperial University for his valuable advice in our researches, and also to the Department of Education and the School for their financial aid throughout our present studies.

Dyeing Department, Tokyo Higher Technical School.

(1) This journal, 1 (1926), 262 & 265.

(2) Ibid., 2 (1927), 233 & 234.

(3) Ibid., 2 (1927), 256.

THE GOLDEN JUBILEE OF THE CHEMICAL SOCIETY OF JAPAN

The Chemical Society of Japan originates in the "Kwagakukwai" (Chemical Society), the first general meeting of which was held on April 26, 1878, at the Professors' Common Room of the University of Tokyo. Soon after the Restoration of 1868, modern sciences were introduced into this country, and in 1873, several courses of special education were established in Tokyo Kaisei Gakko (Tokyo Enlightenment School), the forerunner of the University of Tokyo and a college of an American model. In 1877, Tokyo Kaisei Gakko was reorganized to the University of Tokyo, and graduates were admitted to their degrees for the first time in that year. In the next year, the graduates and students of the Chemistry Course of the Department of Science of this University organized the Chemical Society referred to above. The first President was the late Dr. Mitsuru Kuhara, a graduate of 1877, and later Professor of Organic Chemistry and sometime President of the Imperial University of Kyoto. The word Tokyo was added to the name of the Society soon after, and it was changed to Japan since 1921, to make the name fit for wider scope of the activity of the Society.

As the papers communicated to the Society at its first meeting the following are recorded: viz., "An idea of sanitary chemistry and the necessity of its progress in Japan" by M. Kuhara, and "On Graebe's remarkable achievement regarding artificial alizarine" by E. Watanabe. First of these two was continued at the second meeting held on May 17, when another paper, "The manufacture of Japanese paper" by S. Imai, was also read. On looking upon these subjects we can imagine how eager were those who established this Society to try to do some researches in those early days when exact sciences were just introduced into this country, and laboratory equipments were very meagre. Unhappily the Society not having its publications on those days, the text of these papers cannot be approached now.

The first number of the publications of the Tokyo Chemical Society appeared in February 1880, as the Vol. I, No. 1 of the "Tokyo Kwagakukwaishi" (Journal of the Tokyo Chemical Society). The Journal was quarterly until 1887, and during 1888-1903 ten numbers were published every year. Since 1904 it is monthly. In 1921, the name of the Journal was changed to "Nippon Kwagakukwaishi" (Journal of the Chemical Society of Japan), as the name of the Society was so changed. From the beginning this Journal has been published in Japanese language, and contains original papers communicated to the Society, abstracts of chemical

papers published in other journals, miscellaneous notes, proceedings of the Society, etc. In 1926, another publication "Bulletin of the Chemical Society of Japan" was launched. This Bulletin is printed in English, French or German language and contains the papers communicated to the Society, original or translation of those in Japanese, as well as abstracts of papers published in Japan.

Another publication of the Society is "Kwagaku Yakugoshu" (English-Japanese Dictionary of Chemical Terms) published in 1891. It was out of print for a long time. Meanwhile, Professors Takamatsu and Sakurai, with their friends, compiled and published "Kwagaku Goi" (A Vocabulary of Chemical Terms) in 1900, the second and third editions of which appeared in 1906 and 1918 respectively, with revisions and additions each time. Now in commemoration of the jubilee of this Society, the enterprise was again taken up by the Society, the authors of the latter work having presented its copyright to the Society. New edition of the Vocabulary will be issued in a near future, and French will be added also to English, German and Japanese in its present edition.

The Chemical Society of Japan administers three special funds besides its general fund: viz., Sakurai Fund, Ikeda Fund and Osaka Fund. The Sakurai Fund was donated to the Tokyo Chemical Society in 1908 by the friends and pupils of Professor Joji Sakurai, now President of the Imperial Academy and of the National Research Council of Japan and Emeritus Professor of the Imperial University of Tokyo, to commemorate his completion of twenty-five years as Professor of Chemistry in that University. The income of this fund is to be used in awarding the Sakurai Medal with an honorarium to the author of meritorious papers in the Society's Journal or any other publications. The first recipient of this Medal in 1910 was Prof. M. Ogawa, now President of the Tohoku Imperial University at Sendai, and the second in 1911, Prof. U. Suzuki, now Dean of the Faculty of Agriculture in the Imperial University of Tokyo. The Ikeda Fund is a fund contributed by the friends and pupils of Professor Kikunae Ikeda in 1925, to commemorate his sixtieth birthday and his service as the Professor of Physical Chemistry in the Imperial University of Tokyo. The income of this fund is to be used for assisting scientific publications, and the fund itself may be expended if necessary. The Osaka Fund was presented to the Society by Professor Yukichi Osaka in 1927, from the sum contributed by his friends and pupils to commemorate his sixtieth birthday and his service as the Professor of Physical Chemistry in the Imperial University of Kyoto, another part of this sum having been devoted to assist the publication of "Sexagint," a collection of papers dedicated to him by his pupils on that occasion. The income of this fund as well as the fund itself may be

expended for the promotion of chemistry by any method the Council of the Society decides fit.

In the domain of the international relations following points may be enumerated. First, when the International Committee on Atomic Weights was formed in 1899, Tokyo Chemical Society nominated Professors Sakurai and Ikeda as its representatives. In this point, perhaps it may be added that they addressed an open letter (*Chem. News*, **89** (1904), 305) to Prof. F. W. Clarke, Chairman of the Sub-Committee, criticising the policy of adopting both oxygen and hydrogen standards, and whether in consequence of this letter or not, the oxygen standard has since become the only official standard of International Atomic Weights. The second is the nomination of Professor Osaka as a member of the International Committee for the publication of "Annual Tables of Constants and Numerical Data: Physical, Chemical and Technological." This Committee is an outcome of a resolution passed at the Seventh International Congress of Applied Chemistry, held in London, 1909, and Tokyo Chemical Society, in conjunction with Tokyo Physico-Mathematical Society, Society of Chemical Industry and Agricultural Society, elected Professor Osaka as the Japanese member of the International Committee, and tried to collect necessary data and send them to the General Secretary at Paris, as well as making some donations. The third is the joining to the International Association of Chemical Societies. This Association was formed in 1911, and consisted of one representative Society from each country, and Tokyo Chemical Society joined it in 1912. Perhaps it may be added that all these three were since absorbed in the International Union of Pure and Applied Chemistry, formed together with the International Research Council in 1919. The International Association of Chemical Societies was declared dissolved at the first Conference of the International Union of Pure and Applied Chemistry, held in Rome, 1920. The publication of the Annual Tables of Physico-Chemical Constants and Numerical Data was annexed to the Union at the same meeting, but Professor Osaka is still working as a member of the International Committee for its Publication. The International Committee on Atomic Weights was also affiliated to the Union at that meeting, and was reorganized to the International Committee on Chemical Elements in 1921. The representation of Japan in the International Research Council and the affiliated Unions is assumed by the National Research Council, established as a Government institution in 1921, and although this Council is now working as a self-governing and self-co-opting body, on its first formation the Chemical Society of Japan nominated two members of the National Research Council as its representatives in the persons of Professors Ikeda and Suzuki.

As mentioned in the beginning of this short note, the Chemical Society of Japan is an out-growth of the "Chemical Society" established in 1878, and just completes fifty years of its existence. The number of its original members was 24, while its present strength is 1407 (2 Honorary Members, 710 Fellows and 695 Associates). Of the 24 original members, we can happily count six among our present Fellows: viz., Prof. T. Takamatsu, this year's President of the Society, and Drs. Y. Hiraga, T. Ishido, Y. Koga, I. Nakazawa and H. Yoshida. Hearty congratulations of the Society must be offered to them!

Koichi MATSUBARA.

Addendum. The minutes of the Twenty-fifth Anniversary Meeting of the Tokyo Chemical Society, held on May 9, 1903, appears in *Chemical News*, **87** (1903), 310. The Eighth Annual Meeting, held on April 10, 1886, is also reported in the same journal (*Chem. News*, **53** (1886), 284). Papers read before the Chemical Society of Japan at the monthly and annual meetings since January of 1927 are noticed in the Bulletin of the Society, Vol. II, No. 5, and the following parts.

THE PRECIPITATION OF THE GOLD AND THE SILVER FROM THEIR DILUTE SOLUTIONS.

By Mataichi YASUDA.

Received February 20, 1928. Published May 28, 1928.

It is well known that the precious metals precipitate from their solutions by contact with the base metals. It is also known that the metallic couples such as zinc-copper, zinc-lead and others were studied as reducing agents⁽¹⁾ and lead-aluminium couple was used to precipitate gold for analytical purposes.⁽²⁾ It seems probable that the higher electric potential difference between the metals is more favourable to precipitate the precious metals from their exceedingly dilute solutions such as sea water. As was described in the former paper⁽³⁾, I believe that the gold and the silver in sea water exist in ionic states, thus Au^{+++} , Au^+ and Ag^+ . The metallic couples, therefore, may apply to precipitate the precious metals in this case.

The fact that the precious metals exist in sea water was known very early times, and since then many works were published on this subject.⁽⁴⁾

Since two years I have studied the chemical properties of metallic manganese, and found that this metal is suitable to precipitate the precious metals from exceedingly dilute solution such as sea water, because of its close resemblance to the metallic magnesium, and its chemical reactions is much slower in the sea water than the latter.

At first I tried with a couple of manganese and lead. It is, however, very difficult to obtain the couple directly by dipping the metallic manganese in the solution of lead, for the adhered lead on the manganese has spongy appearance and is easily detached therefrom. I, therefore, made an alloy by mixing the manganese and the lead. The purpose of the metallic couple or alloy is to utilize the galvanic current which occurs between these metals, the easily oxidizable metal, the manganese, being anode, and the nobler

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- (1) J. J. Hood, *J. Soc. Chem. Ind.*, **14** (1895), 808; Christy and Butters, *Chem. News*, **75** (1897), 309; H. Becker, *Chem. Zeit.*, **21** (1897), 296.
 - (2) *Proc. Chem. Met. a. Min. Soc. South Africa*, Sept. 1913.
 - (3) M. Yasuda, this journal, **2** (1927), 322.
 - (4) Malaguti and Durocher, *Compt. rend.*, **49** (1859), 463; Liversidge, *Chem. News*, **74** (1896), 146; A. Münster, *J. Soc. Chem. Ind.*, **11** (1892), 351; Liversidge, *Proc. Roy. Soc. New South Wales*, **29** (1895), 335; Liversidge, *J. Chem. Soc.*, **71** (1897), 298; J. R. Don, *Trans. Am. Inst. Min. Eng.*, **27** (1897), 615; L. Wagoner, *Trans. Am. Inst. Min. Eng.*, **31** (1901), 807; F. Haber, *Z. angew. Chem.*, **40** (1927), 303; J. W. Pack, *Min. and Sci. Press*, **77** (1898), 154; P. de Wilde, *Arch. Sci. phys. Nat.*, 4th ser. **19**, 559; A. Wiesler, *Z. angew. Chem.*, **19** (1906), 1795; H. Koch, *Kolloid Z.*, **22** (1918), 1.

metal, the lead, cathode. The galvanic current will continue until the anode is oxidized and is covered by the film of mangano-manganese oxide. By this galvanic current the precious metals in sea water will deposit on the cathode metal, lead.

As above stated, the gold which is able to effect the galvanic current is the ions, Au^{+++} and Au^+ . The chlorine ion oxidizes the manganese and the gold deposited on the lead. The silver will behave the same as the gold. The manganese can change its valency in several stages, and form many oxides, some of which are soluble and others insoluble as was described by Spring and de Boeck⁽¹⁾. If we put the manganese-lead couple into the sea water, no perceptible change in the solution was found at beginning, but after some hours the soluble hydroxide is oxidized, and hydrated black mangano-manganic oxide adhered on all parts of the vessel.

It may be also supposed as J. M. Stuart and G. D. Bengough⁽²⁾ stated, the manganese hydroxide which is formed from the manganese charged positively in colloidal state and neutralized the ion AuCl_4^- and changes to single salt AuCl_3 or AuCl , and the metallic ions Au^{+++} or Au^+ neutralized again with negatively charged metal and is deposited on the lead. Here the passivity of the metallic manganese which is known to be very unstable, and soon recover its electric potential and the reactions go on.⁽³⁾ In general it is recognized that the metal resemble to zinc or magnesium in its behaviors.

At first, I have carried out the experiments on several couples of metals, such as copper-manganese, manganese-lead and lead-aluminium. The preparation of the alloys of lead and aluminium⁽⁴⁾ or lead and manganese⁽⁵⁾ are very difficult, but the mechanical or heterogeneous mixtures of lead and aluminium or lead and manganese can easily be prepared. The experiment on lead-manganese couple was carried out in the following manner.

The powdered lead and manganese are put together in a steel case and are strongly hammered with an air hammer as hard as possible, and at last a thin plate of 0.07 mm. thickness was obtained. The plate thus made was then cut into rectangular sheet and hang into a beaker in which two or three litres of sea water being contained, and stir the water with a appropriate stirrer. After some hours, the plate is taken out and rolled to a small volume and put in a crucible. Then 2 or 3 grammes of lead oxide are added and heated to a fused state to oxidise the remaining manganese in the alloy,

(1) Spring and de Boeck, *Bull. soc. chim.*, [2] **48** (1887), 170.

(2) J. M. Stuart and G. D. Bengough, *Chem. News*, **161** (1922).

(3) H. Küssner, *Z. Elektrochem.*, **16** (1910), 758.

(4) A. G. C. Gwyer, *Z. anorg. Chem.*, **57** (1908), 149.

(5) R. S. Williams, *Z. anorg. Chem.*, **55** (1907), 91.

and obtained a button and cupelled. The gold or the silver-gold bead thus obtained is weighed, and then dissolved in nitric acid (specific gravity, 1.18), and the remaining gold is washed with water, dried, heated and weighed as usual manner. It was confirmed that the initial lead-manganese couple contains no silver or gold by cupellation four times.

To test the accuracy of the method, artificially made sea waters were used, which contained some sodium chloride, potassium chloride, magnesium sulphate and potassium sulphate as well as known quantities of gold chloride. The results are given in the following table.

TABLE 1.

Solution	Gold added gr./l.	Temp.	% of Mn in alloy	Surface of alloy sq. cm.	Wt. of alloy gr.	Duration of exp. hr.	Gold obt. gr.	% of gold obt.	Gold calc. for 1000 kg. alloy gr.
Aq. sol.	2.7×10^{-4}	15°	2	18.00	1.3749	5	1.15×10^{-4}	19.7	81.7
Aq. sol.	"	28°	2	17.96	1.4087	28	0.65 "	11.6	42.2
Sal. wat.	"	18.5°	"	53.90	4.2940	69	3. "	53.8	64.3
Sal. wat.	3×10^{-4}	18.5°	"	27.72	1.4824	69	3. "	50.0	20.2

The volume of solution used in the experiment = 2 litres.

Aq. sol. = aqueous solution.

Sal. wat. = saline water.

Next, the natural sea water was tested which had been obtained at a point four miles off the coast of Kominato Bay, south eastern sea from Tokyo. The results are as follows.

TABLE 2.

% of Mn in alloy	Surface of alloy sq. cm.	Wt. of alloy gr.	Total duration of exp. hr.	Gold-silver bead obt. gr.	Gold obt. gr.	Gold calc. for 1000 kg. alloy gr.
8%	28.50	2.0284	641	27×10^{-6}	0.68×10^{-6}	3.4
8%	28.42	2.1000	641	77×10^{-6}	—	—
9.05%	34.40	4.9255	467	85.5×10^{-6}	—	—

Three litres of sea water was used each time, and after some hours it was thrown away and fresh sample of three litres of sea water was introduced into the vessel, and so on. By this manner the water was changed six times in each experiment, so in total eighteen litres of sea water was used. The weight of the bead, therefore, was obtained from 18 litres of the sea water.

Next, some excess gold was added to the Kominato Bay sea water and the gold content was raised to 37 mg. per one cubic meter, and the experiments were done using couples of various contents of manganese. The results are as follows.

TABLE 3.

% of Mn in alloy.	Thickness of alloy mm.	Surface of alloy sq. cm.	Weight of alloy		Wt. of Au-Ag bead gr.	Wt. of gold gr.	Gold adhered on 1 sq. cm. of alloy gr.
			Before exp. gr.	After exp. gr.			
1	0.193	24.38	1.3384	1.3280	10×10^{-6}	—	—
2	0.100	20.30	2.0307	1.9994	10.7 "	3.4×10^{-6}	0.17×10^{-6}
2	0.100	40.80	2.1191	—	16.5 "	6.6 "	0.16 "
3	0.075	36.40	1.5621	1.4984	31.7 "	9. "	0.27 "
4	0.113	26.40	1.6998	1.7109	390. "	18. "	0.68 "
4	0.156	30.32	2.7317	2.7552	770. "	30. "	0.97 "
4	0.130	99.76	7.5199	7.5656	113. "	43. "	0.43 "
5	0.060	46.00	1.6604	1.6649	80. "	15. "	0.32 "
6	0.096	42.78	1.8518	1.8396	34.2 "	10. "	0.25 "

The durations of these experiments were 100 hours, the temperatures, 10–20° C., and the volumes of the sea water, three litres. From these experiments it seems that the 4% alloy gives best result. The weight of alloy decrease in some cases, for the manganese oxidized and removed as oxide or hydroxide from the plate. I have collected the precipitate settled down to the bottom of the vessel, and obtained two samples, about 0.5 gr. in each case, and wrapped with a lead foil and heated with lead oxide in a crucible, and obtained a button and cupelled. In this way, a bead of gold or silver was not obtained. So it is clear that the gold or silver does not precipitate with the oxide or hydroxide of manganese.

Next, another experiment was done with sea water taken at Atami Bay which contained 3 mg. of gold in a cubic meter. And moreover, the experiments were extended to the waters which were made by adding some gold chloride to the Atami Bay water. The results are as follows :

TABLE 4.

Gold content mg. in cb. meter	Thickness of alloy mm.	Surface of alloy sq. cm.	Weight of alloy		Gold adhered gr.	Gold adhered on 1 sq. cm. gr.	Water
			Before exp. gr.	After exp. gr.			
3	0.07	37.4	2.6074	2.5232	2.3×10^{-6}	0.06×10^{-6}	Natural sea water AuCl ₃ was added
7	0.055	47.32	2.5440	2.5215	5. "	0.1 "	
7	0.075	56.40	2.3453	2.3375	5.8 "	0.1 "	
10.5	0.055	60.52	2.7027	2.6843	38. "	0.6 "	
10.5	0.075	54.88	3.3650	3.3635	19.6 "	0.35 "	
17.5	0.055	36.64	2.0430	2.0180	30.7 "	0.85 "	
17.5	0.075	74.46	4.1990	4.1950	17.5 "	0.32 "	
22.9	0.055	56.48	2.3032	2.3000	12.3 "	0.22 "	
22.9	0.075	89.60	5.7268	5.7068	29. "	0.33 "	
37	—	—	—	—	—	0.69 "	"

In these experiments an alloy of 5% manganese was used. Three litres of the waters were taken, the temperature of which was 23°C., and the duration of each experiment was 122 hours.

Theoretical Considerations. We will assume that an alloy plate is moving in the undisturbed solution containing some gold atom. The number of the gold atoms can be calculated as follows. It is known that 6×10^{23} atoms (Avogadro's number) exist in 179.2 grammes of gold. So the number of gold atoms in the sea water which contains a mg. of gold in one cubic meter is $6 \times 10^{23} \times a \times 10^{-3} / 179.2 = 3.07 \times 10^{18} \times a$. It becomes, therefore, in one cubic centimeter, $3.07 \times a \times 10^{12}$, and the gold atoms come to one square centimeter, or one side of the cube are,

$$(3.07 \times 10^{12} \times a)^{\frac{2}{3}} = 1.486 \times 10^8 \times a^{\frac{2}{3}}.$$

This is the number of gold atoms sweep over the metallic surface of one square centimeter and adhere on the surface. On the other hand, the weight of the single atom of gold is, $197.2 \times 1.66 \times 10^{-24} = 0.33 \times 10^{-21}$ gr., where 1.66×10^{-24} is the weight of one atom of hydrogen. So the weight of gold sweep over the unit area of alloy surface is

$$0.33 \times 10^{-21} \times 1.486 \times 10^8 \times a^{\frac{2}{3}} = 0.49 \times a^{\frac{2}{3}} \times 10^{-13} \text{ gr.}$$

If we suppose that the sea water contains 32 mg. gold in one cubic meter, or $a = 32$, then the above quantity becomes 4.94×10^{-13} gr.

Assume the metallic surface moves in the water with the velocity of n centimeter per second and there precipitated b gr. of gold during h hours, then,

$$b = 4.94 \times 10^{-13} \times n \times h \times 3600 \text{ gr.}$$

Now taking $n = 3$, and $h = 100$, it becomes,

$$b = 0.54 \times 10^{-6} \text{ gr.}$$

This number approximately agrees with the experimental results. In the present experiment the water was stirred constantly with a stirrer, so the concentration of the gold decreases with time. Moreover, the factors such as the free path of ions, hydrodynamic conditions of flowing water on the surface and the influence of temperature must be considered. The above calculations, therefore, by no means an exact one, but only rough approximation.

It is probable that the colloidal gold in the sea water adheres also on the metallic plate for the particles have electric charges.

Summary.

It has been pointed out that the metallic alloy of manganese and lead is suitable to fish the gold from its very dilute solution such as sea water. The method of preparation and the composition of the alloy have been described. The efficiency of its action has been studied.

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APPLICATION OF AN ELECTROMAGNETIC FORCE TO "THERMOBALANCE."

By Zen-ichi SHIBATA and Masaji FUKUSHIMA.

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Introduction. The "thermobalance" invented by Prof. Honda⁽¹⁾ has wide applications in chemical and metallurgical experiments. But, to our regret, the following defects are met with in its use. (1) By magnifying the sensibility of the balance, the movements on its scale are multiplied even by a small change of weight, and hence it is necessary to interrupt the measurement and change its weight, on the beam of the balance during an experiment. (2) And during this manipulation, the change in the weight of a sample cannot be measured. (3) As the up and down movements of the arms of the balance cause the spring to stretch and contract, the hysteresis of the spring causes an error. (4) The thermocouple cannot be fixed with the sample, so that when the position of the latter is displaced by the change in its weight, it recedes from the former, and the exact reacting temperature is not observable by the thermocouple.

To remedy the above obstacles, the present writers made the following improvements by using an electromagnet.

In our improved apparatus, a current is adjusted in the observing position so that the scale is always set at the zero point. The change in the weight of the sample can be indirectly found from the amount of the current, the sensibility can be magnified, the hysteresis eliminated, and the temperature of the reaction can be found exactly.

Apparatus and Manipulation. The "thermobalance" used in this experiment was that invented by Prof. Honda, and an electromagnet was attached to one side of the beam.

(1) Honda, *Science Reports of the Tohoku Imperial University*, 4 (1915), 97.

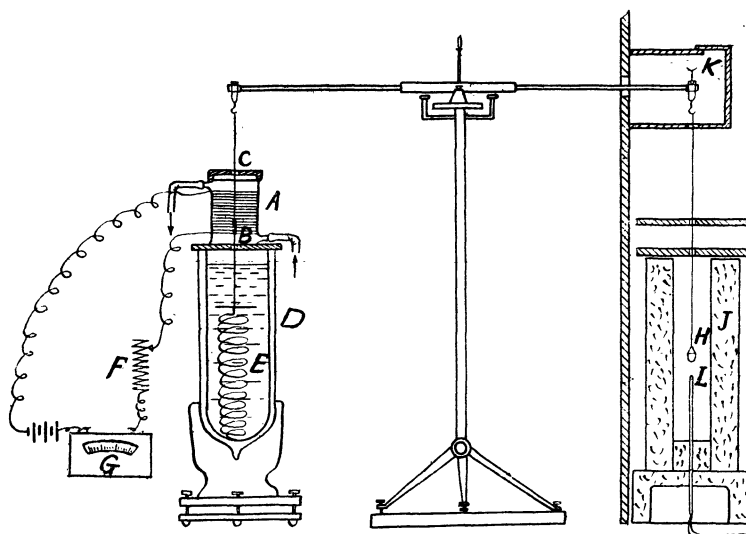


Fig. 1.

Fig. 1 shows the apparatus in which A is a coil wound with silk-wrapped copper wire on a glass cylinder 4.7 cm. in diameter and 6 cm. in length. It is double-walled, and between the walls water is passed to avoid the heating by the current. C is a brass cap and in its centre a small hole is bored, through which passed a slender copper wire. The upper end of the wire is fixed to one arm of the balance and the lower bound to the damper plate, passing through a mild steel rod B, which is 0.4 cm. in diameter and 1.4 cm. in length. Under the plate the upper end of the spring E is fixed. The sensibility of the balance is intensified by using a somewhat weak spring and a less viscous oil, mixed an equal volume of the transformer oil with the petroleum. B is placed downwards from the centre of the coil, to pull it upwards, when the current is passed. The

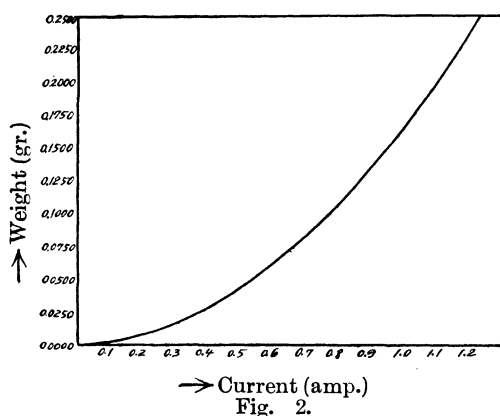


Fig. 2.

The current was lead from a 6 volt battery, and observed with an exact ammeter. The adjustment of the current is easily made by several slide resistances. L is a thermocouple and J a furnace. The parts hatched protect the apparatus from the vibration of the balance by a convection current of air.

In order to obtain the relation between the current and the

weight, 0.3 gr. of the weight is placed on K, and riders on the other side of the arm, to keep the scale at zero, and then on decreasing the weight on K we determine the amount of current sufficient to keep the scale at zero. The results are shown in Table 1 and Fig. 2.

TABLE 1.

Weight gr.	Current amperes	Weight gr.	Current amperes	Weight gr.	Current amperes
0.0000	0.000	0.0700	0.640	0.1600	0.982
0.0010	0.053	0.0750	0.664	0.1650	0.997
0.0020	0.087	0.0800	0.687	0.1700	1.014
0.0030	0.112	0.0850	0.708	0.1750	1.029
0.0050	0.152	0.0900	0.730	0.1800	1.043
0.0080	0.199	0.0950	0.751	0.1850	1.058
0.0100	0.225	0.1000	0.772	0.1900	1.074
0.0150	0.283	0.1050	0.791	0.1950	1.087
0.0200	0.331	0.1100	0.812	0.2000	1.102
0.0250	0.392	0.1150	0.829	0.2050	1.116
0.0300	0.412	0.1200	0.846	0.2100	1.130
0.0350	0.445	0.1250	0.864	0.2150	1.143
0.0400	0.475	0.1300	0.882	0.2200	1.154
0.0450	0.508	0.1350	0.898	0.2250	1.167
0.0500	0.537	0.1400	0.915	0.2300	1.181
0.0550	0.563	0.1450	0.932	0.2350	1.193
0.0600	0.591	0.1500	0.949	0.2400	1.207
0.0650	0.615	0.1550	0.965	0.2450	1.219
—	—	—	—	0.2500	1.232

Results of Experiments. To determine the accuracy of the improved "thermobalance" the present writers determined the decomposition curves of the following five compounds of "Kahlbaum zur analyse."

The thermocouple used was calibrated in the range 300–1200°C. with the Pt-PtRh thermocouple which was certificated at the "Deutsche physikalische-technische Reichsanstalt," and below 300°C. calibrated with the boiling points of water and naphthalene. In the following figures, the ordinates represent the decrease of the weight of the sample, and the abscissa the temperature. The shapes of the decomposition curves are of course somewhat liable to the heating velocity. In the present experiments, it was generally 2 degrees per minute, and at the point where a vigorous decomposition took place 1 degree or less per minute.

Calcium carbonate, CaCO_3 . The decomposition curve of calcium carbonate is shown in Fig 3 (B). Its decomposition begins at about 400°C., reaches a maximum at 700°C., and finishes at 780°C. to become CaO . The calculated and the observed values of decomposed CO_2 are given below.

CaCO ₃	CO ₂		
	Calculated value	Observed value	Error
0.3175	0.1396	0.1399	+0.0003

Copper sulphate, CuSO₄·5H₂O. The decomposition curve for the copper sulphate is shown in Fig. 3 (A). The stage of the decomposition is denoted as follows.

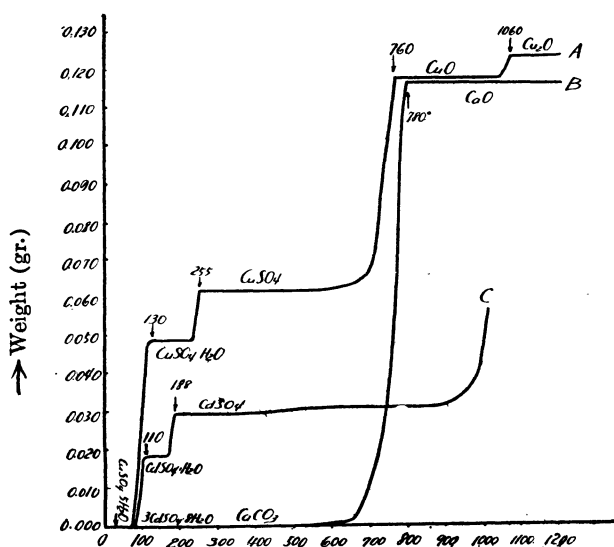
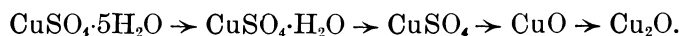


Fig. 3. → Temp. (°C.)

The first stage of the reaction occurs at 75–120°C. four molecules of water being removed and one remaining molecule of water escapes at 230–255°C. The anhydrous salt begins to decompose gradually at 600°C. evolving SO₃, and at 760°C. it changes completely to CuO and on further heating it is decomposed to Cu₂O at 1040–1060°C.

The observed data are shown in the following table.

CuSO ₄ ·5H ₂ O	4H ₂ O	H ₂ O	SO ₃	$\frac{1}{2}\text{O}_2$
0.1723	Calculated value 0.0497	Calculated value 0.0124	Calculated value 0.0553	Calculated value 0.0055
	Observed value 0.0495	Observed value 0.0127	Observed value 0.0556	Observed value 0.0060
	Error –0.0002	Error +0.0003	Error +0.0003	Error +0.0005

Cadmium sulphate, 3CdSO₄·8H₂O. The decomposition curve of this salt is shown in Fig. 3 (C). Cadmium sulphate leaves its crystallising water at two stages, 80–110°C. and 170–190°C. On elevating the temperature, the anhydrous salt begins to decompose at 900°C. The observed data are as follows:—

3CdSO ₄ ·8H ₂ O	5H ₂ O			3H ₂ O		
	Calc. val.	Obs. val.	Error	Calc. val.	Obs. val.	Error
0.1614	0.0189	0.0186	+0.0003	0.0113	0.0113	0.0000

Barium chloride, BaCl₂·2H₂O. The decomposition curve of barium chloride is shown in Fig 4 (D). This salt loses one molecule of water at 70°–100°C. and then its weight begins gradually to decrease above 500°C. The observed data are as follows:—

BaCl ₂ ·2H ₂ O	H ₂ O			H ₂ O		
	Calc. val.	Obs. val.	Error	Calc. val.	Obs. val.	Error
0.2581	0.0191	0.0190	−0.0001	0.0191	0.0192	+0.0001

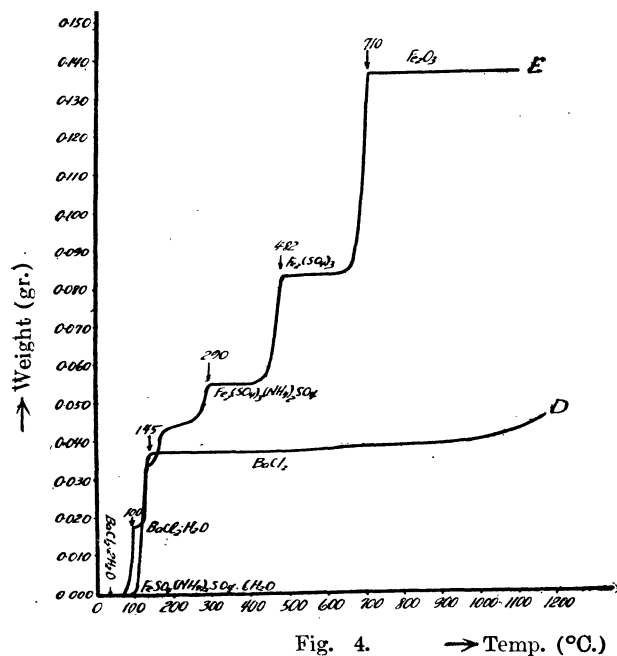


Fig. 4. → Temp. (°C.)

Mohr salt, FeSO₄(NH₄)₂SO₄·6H₂O. The decomposition curve of this salt is shown in Fig. 4 (E). The crystallising water is removed at 100°C., one part of ammonia is given off and at the same time is oxidised to ferric salt at 170°C. At 290°C. it becomes Fe₂(SO₄)₃(NH₄)₂SO₄, at 420–490°C. (NH₄)₂SO₄ is lost remaining ferric sulphate, and at 650–710° decomposes to ferric oxide. The observed results are as follows:—

FeSO ₄ (NH ₄) ₂ ·SO ₄ ·6H ₂ O	6H ₂ O + NH ₃			(NH ₄) ₂ SO ₄			SO ₃		
	Cal.	Obs.	Err.	Cal.	Obs.	Err.	Cal.	Obs.	Err.
0.1700	0.0547	0.0553	+0.0006	0.0286	0.0287	+0.0001	0.0521	0.0528	+0.0007

Summary.

The present writers have applied an electromagnet to the "thermo-balance" to remove the previous defects and succeeded in elevating its sensibility to that of the chemical balance. To determine its accuracy, the decomposition curves of the following five compounds have been determined: calcium carbonate, copper sulphate, cadmium sulphate, barium chloride and Mohr salt.

In conclusion, the authors express their hearty gratitude to Prof. Oishi and Prof. Murakami for their kind directions.

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ÜBER NEUE ARBEITEN AUF DEM GEBIETE DER BESTIMMUNG DER STABILITÄT VON RAUCHLOSEM PULVER.

Von Michael TARLÉ.

Eingegangen am 7. April 1928. Ausgegeben am 28. Mai 1928.

In der letzteren Zeit sind wieder einige Arbeiten über abgeänderte bzw. neue Untersuchungsmethoden der Stabilität veröffentlicht worden. Das Interesse, welche diese Frage hervorruft, ist leicht verständlich. Die Stabilität—oder chemische Beständigkeit—ist eine Eigenschaft, welche von grosser Bedeutung für das Herstellungsverfahren und für das Lagern des Pulvers ist. Es gibt aber bis jetzt noch keine Untersuchungsmethode dieser Eigenschaft, welche man als einwandsfrei ansehen könnte.

Man kann im allgemeinen die gegenwärtig benutzten Methoden in zwei Hauptklassen teilen; die erste—die qualitative—besteht in der Feststellung der Zeit, welche nötig ist um damit ein Reagenzpapier von den bei Zerlegung des Pulvers auftretenden Gasen gefärbt wird. Die andere Prüfungsart, welche man als quantitativ bezeichnen kann, besteht im Auffangen und in der Bestimmung der Zerfallprodukte während einer bestimmten Zeit. Zu dieser Klasse gehört auch die Probe, welche u. a. bei dem Amerikanischen Militäramt angewendet wird, und welche in der Bestimmung des Gewichtsverlustes bei einer gewissen Temperatur besteht. Zu derselben Klasse gehört ebenso die Manometrische Probe von Obermüller die Bestimmung des Druckzuwachses, welcher durch die beim Erhitzen des Pulvers auftretenden Gase hervorgerufen wird. Alle diese Proben

leiden an verschiedene Mängel. Zunächst werden sie bei verhältnismässig hohen Temperaturen vorgenommen, da bei gewöhnlicher Temperatur die Zerfallsgeschwindigkeit des Pulvers kleine Werte hat und die Versuche sehr viel Zeit in Anspruch nehmen würden. Das wäre aber aus praktischen Gründen unbequem; ausserdem ist es schwer, bei einen lange dauernden Versuch die Versuchsbedingungen konstant zu halten.

Wenn man, zwecks Reaktionsbeschleunigung, zur Temperaturerhöhung greift, stösst man auf eine neue Schwierigkeit; bei einer hohen Temperatur verdampfen das Lösungsmittel und das im Pulver enthaltene Wasser, die Zerfallreaktion muss also eine andere sein, wie bei normaler Temperatur; die Zusammensetzung der Zerfallprodukte ist auch wahrscheinlich eine andere. Es ist eigentlich unzulässig, auf Grund von Versuchen, welche bei einer hohen Temperatur vorgenommen wurden, auf die Stabilität unter normalen Verhältnissen zu schliessen. Der beste Beweis dafür ist der Umstand, dass die Versuche nach verschiedenen Prüfungsmethoden vorgenommen, oft keine übereinstimmende Resultate liefern. Auch kennt man Fälle, wo ein "stabil" gefundenes Pulver augenscheinlich ohne Ursache plötzlich explodierte... Bei den meisten Untersuchungsverfahren (ausser den Gewichtsverlust- und manometrischen Methoden) werden die entbandenen nitrosen Gase qualitativ entdeckt oder quantitativ bestimmt. Es ist fraglich, ob man in dieser Weise die chemische Beständigkeit und die Zerfallsgeschwindigkeit studieren kann. Die Zersetzungsprodukte bestehen doch nicht nur aus NO_2 und NO , sondern, ausser denselben, aus CO , CO_2 , Wasser, Ameisensäure, Oxalsäure, Oxybrenztraubensäure usw.⁽¹⁾ Z. B., in den Seeminen, welche hermethisch geschlossen 7 oder 8 Jahren lagen, hat man folgende Gase gefunden:⁽²⁾

O_2	0.3%	H_2	6.5%
CO_2	2.1	N_2O	1.5
CH_4	0.5	N_2	88.9

Man darf also mit Sicherheit annehmen, dass bei verschiedenen Temperaturen die autokatalytische Reaktion verschieden verläuft und dass das Auffangen der nitrose Gasen beim weitem nicht, genügt um in das Wesen dieser Reaktion einen klaren Einblick zu bekommen und um die chemische Beständigkeit mit einiger Sicherheit bestimmen zu können. Es ist bemerkenswert, dass die neueren Arbeiten auf diesem Gebiete sich hauptsächlich mit Gewichtsverlustmethoden beschäftigen. Der Vorteil dieser Methoden besteht in dem Umstande, dass hierbei sämtliche Zerfallprodukte angezeigt werden; zur Messung der Reaktionsgeschwindigkeit eignet sich

(1) Brunswick, "Das Rauchlose Pulver", 1926, S. 353.

(2) Vieille, Mémorial des Poudres et Salpêtres, 15 (1910), 63.

das Verfahren jedenfalls besser, als die übliche Bestimmung eines einzelnen Gases, wie NO_2 . Das andere Übel—die hohe Versuchstemperatur—bleibt vorläufig bestehen.

Die Arbeit von v. Meerscheidt-Hüllessem hatte zum Zwecke die Konstruktion eines Apparates, welcher erlaubt hätte das Gewichtsverlust des Pulvers bequem zu beobachten⁽¹⁾. Die Versuche wurden bei 115° , 8 Stunden täglich vorgenommen und dauerten 8 Tage. Es lassen sich zugleich 37 Muster untersuchen. Der Apparat soll bequem, gefahrlos, ökonomisch und genau arbeiten.

Eine andere vor Kurzem erschienene Abhandlung⁽²⁾ befasst sich mit derselben Methode und bietet ebenfalls prinzipiell nichts neues an. Die Versuche werden bei etwa 110° vorgenommen und dauern 72 Stunden (9 Tage). Vor dem eigentlichen Versuch werden die Pulvermuster 8 Stunden in offenen Gläsern erhitzt (die Temperatur ist nicht angegeben) um die Reste des Lösungsmittel zu entfernen. Da dabei auch teilweise die Zerfallprodukte entweichen, kann man nicht, streng genommen, die Versuche als quantitativ bezeichnen. Im besten Falle können sie zu Ermittlung der Vergleichswerte dienen.

Zur Messung der Zerfallgeschwindigkeit bei normaler Temperatur (bis etwa 50°), auf die es gerade ankommt, können die bereits besprochenen Methoden nicht angewendet werden. Einen anderen Weg zur Aufklärung dieser Frage versuchen Ryan und Lantz⁽³⁾ zu finden, indem sie bestrebt sind, den Temperaturkoeffizienten der Zerfallreaktion zu ermitteln. Der Gedanke ist sehr interessant und wird möglicherweise in Zukunft (die Arbeit wird fortgesetzt) fruchtbringend sein; vorläufig scheint es noch bedenklich, die Versuche als eine Stabilitätsprobe "temperature coefficient test" wird sie von den Verfassern genannt) zu betrachten. In einen besonders konstruierten Apparat wurde Luft durch die erhitzten Nitrozelluloseproben geschickt und das von dem Luftstrom während einer bestimmten Zeit mitgenommene Stickstoffdioxid von einer KI-Lösung wurde absorbiert. Das ausgeschiedene Jod wurde elektrometrisch bestimmt. Die Versuche wurden bei drei Temperaturen— $99.5-100^\circ$, $116-118^\circ$ und $136-140^\circ$ —vorgenommen. Die Versuchsdauer beträgt 2 bis 3 Stunden bei der höchsten und etwa 24 Stunden bei der niedrigsten Temperatur. Die lange Versuchsdauer im letzten Falle wird auch die Zeit—20 Stunden—, welche nötig ist, um eine gleichförmige Entwicklungsgeschwindigkeit von NO_2 zu erhalten, verursacht. Für die 100° -Versuche braucht man nur 2 Stunden zu warten. Die Titrationen bei 100° -Versuchen wurden nach 4 Stunden, bei 140° nach 30 Minuten vorgenommen.

(1) *Z. ges. Schiess- Sprengstoffw.*, 21 (1926), 137.

(2) Simon Thomas, *Z. angew. Chem.*, 40 (1927), 991.

(3) *Ind. Eng. Chem.*, 20 (1928), 40.

Man kann diese Methodik nicht als einwandfrei bezeichnen. Der Temperaturbereich (99.5-140°) ist nicht zweckmässig gewählt worden, da zwischen 135° und 140° die Reaktionsgeschwindigkeit-Temperaturkurve einen scharfen Knick aufweist⁽¹⁾, was auf eine plötzliche Änderung des Reaktionsverlaufes hindeutet. In der Tat fand Sapojnikoff, dass die Änderung der Zerfallgeschwindigkeit mit der Temperatur—für eine unlösliche Nitrozellulose mit 13.4% Stickstoff—durch die Formel

$$\frac{V}{t} = A + BT$$

ausgedrückt wird, wo V die Vergrösserung des Volumens der Zerfallgase in der Zeiteinheit t , und T die jeweilige Temperatur bedeutet. A und B sind Konstanten. Zwischen 120° und 135° betragen die respektiven Werte von A und B -2.22 und +0.0092, zwischen 135° und 150° -64.22 und +0.48. Wir können also annehmen, dass in der Nähe von 135° eine plötzliche Änderung des Reaktionsverlaufes eintritt.

Ryan und Lantz geben keine Definition für- und berechnen nicht den Temperaturkoeffizienten. Wenn wir die Reaktionsbeschleunigung auf Grund der Versuche von Ryan und Lantz nach der Formel

$$\frac{G_1 : G_2}{T_1 - T_2} = K$$

berechnen, wo G_1 und G_2 die Menge von den entwickelten nitrosen Gasen (ausgedrückt in mg. von Stickstoff pro Stunde pro 1 gr. Nitrozellulose) bei den Temperaturen T_1 und T_2 bedeuten, erhalten wir die folgende Werte, (siehe Tafel).

Es fällt auf, dass in einigen Fällen die Grösse K mit der Temperaturerhöhung sinkt; d. h. dass die Reaktion, statt einer Beschleunigung, eine Verlangsamung erleidet. Für eine autokatalytische Reaktion und für bei nahezu gleichen Temperaturbereichen, kann dies nicht stimmen. Vielmehr weist diese Diskrepanz auf einen Fehler der Versuchsmethodik hin. Vor allem müsste bewiesen werden, dass die Menge der entwickelten nitrosen Gase wirklich ein Mass für die Geschwindigkeit der Zerfallreaktion darstellt. Da die Zerfallprodukte aus mehreren anderen Verbindungen bestehen, und da die Zusammensetzung der Zerfallprodukte sich mit der Temperatur ändert, lässt sich auf diesem Wege die Reaktionsgeschwindigkeit kaum, oder nur qualitativ, verfolgen. Andererseits lassen uns die hohe Versuchstemperatur und das Durchsaugen der Luft, welches die Zerfallgase wegnimmt und infolgedessen höchstwahrscheinlich den Reaktionsverlauf ändert, keine bestimmten Schlüsse auf die wirkliche Stabilität des Pulvers ziehen.

(1) Sapojnikoff, *Mem. Poudr. Salp.* 14 (1906-1907), 42.

Stickstoffgehalt in dem Muster.	G	$T(^{\circ}\text{C})$	K
13.26%	0.61	138	0.37
	0.11	123.2	0.81
	0.0057	99.5	
13.22	0.87	139.2	0.78
	0.050	117.0	0.57
	0.0048	99.5	
13.10	0.74	137.8	0.67
	0.059	118.2	0.59
	0.0054	99.5	
12.86	0.53	136.0	0.56
	0.055	118.7	0.59
	0.0048	99.5	
13.01	0.61	136.0	0.42
	0.118	123.6	0.91
	0.0054	99.5	
13.19	0.71	137.5	0.82
	0.042	117.0	0.58
	0.0041	99.5	
12.13	0.67	137.6	0.79
	0.041	117.0	0.57
	0.0041	99.5	
13.07	0.86	138.7	0.75
	0.051	116.2	0.58
	0.0052	99.3	
13.20	0.85	138.6	0.82
	0.046	116.0	0.56
	0.0048	99.0	
13.25	0.83	138.5	0.71
	0.055	117.2	0.52
	0.0060	99.5	

Eine neue Methode zur Bestimmung des Säuregehaltes des Pulvers schlägt Nie. L. Hansen⁽¹⁾ vor. Er begnügt sich nicht mit der Bestimmung der Nitrosäuren, sondern verfolgt das Anreichern an sämtlichen Säuren, welche durch die Zersetzung des Pulvers entstehen. Es wird nämlich die Wasserstoffionenkonzentration im Wasser, mit welchen die zuvor erhitzte Pulverprobe ausgeschüttelt wurde, gemessen. Da diese Messungen elektrometrisch, unter Anwendung von einer Chinhydronelektrode mit grosser Genauigkeit gemacht werden können, so erlaubt die Methode auch kleine Änderungen des Säuregehaltes zu verfolgen. Die Versuche wurden mit Pulverproben, welche bei 90.5°, 110° und 120° erhitzt worden sind, ausgeführt. Wenn die Versuche auf niedere Temperaturen ausgedehnt werden und somit der Temperaturkoeffizient der Zerfallreaktion einwandfrei bestimmt wird, so wird man ein Mittel erhalten, um ein zuverlässiges Urteil über die Stabilität des Pulvers abzugeben. Vorläufig sind wir noch nicht so weit. Das Interesse aber welches man dieser Frage widmet, bürgt dafür, dass die Lösung des Problems nicht lange auf sich warten lassen wird.

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(1) Cit. nach L. Metz, *Z. ges. Schies- Sprengstoffw.*, 21 (1926), 186.

THE CRYSTAL STRUCTURE OF THIOUREA.

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Introduction. Now that the crystal structure of urea CON_2H_4 has been determined by Mark and Weissenberg,⁽¹⁾ it may be of interest to see if there is any structural relationship between the crystals of this compound and those of an analogous one, thiourea CSN_2H_4 . The present investigation was made on the thiourea crystals by the Laue photographic and the X-ray spectrometric methods, of which the procedure are almost the same as already described in detail in a paper by one of the present authors.⁽²⁾ Groth⁽³⁾ gives the following data concerning the crystals of this compound:

Orthorhombic bipyramidal, $a:b:c = 0.7163:1:1.1155$.

Specific gravity, 1.406.

Cleavage, $b\{010\}$ and $r\{101\}$ perfect.

As to the specific gravity, a value 1.450 considerably deviating from the above is also quoted as obtained in some occasion.⁽³⁾ Hence another determination was made by means of a Westphal balance, which gave 1.407 in good agreement with the first-mentioned value.

The Unit of Structure. Thiourea from C.A.F. Kahlbaum was recrystallized from aqueous solution. In a case of rapid crystallization from somewhat supercooled solution, transparent six-sided plates of a few square millimetres were obtained. A Laue photograph taken with the X-rays⁽⁴⁾ incident normally to the plate showed that this plate was parallel to the crystallographic $c(001)$ plane. In most cases of slow crystallization there grew thick prisms with rhombic bases. Several Laue photographs were obtained with a cleaved slip from the crystal, and it was found that the cleavage plane was $b(010)$. In Table 1 are given the Laue photographic data.

(1) H. Mark and K. Weissenberg, *Z. Physik*, **16** (1923), 1.

(2) I. Nitta, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **4** (1926), No. 47, 49.

(3) P. v. Groth, "Chemische Krystallographie," 3. Teil, (1910), 555.

(4) X-rays from a Coolidge tube with tungsten anticathode.

TABLE 1. Laue Photographic Data.

hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.	hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.
(201)	8.61	0.31	0.1055	mw	{(015)	21.0	0.235	0.0515	f
(211)	9.61	0.295	0.0955	w	{(01 $\bar{5}$)	"	0.20	0.044	f
(031)	9.80	0.295	0.094	f	{(214)	21.6	0.25	0.0535	mw
(221)	12.61	0.26	0.072	w	{(21 $\bar{4}$)	"	0.185	0.0395	m
(231)	17.61	0.225	0.054	s	{(312)	21.8	0.25	0.0535	ms
(301)	18.35	0.215	0.0505	vs	{(31 $\bar{2}$)	"	0.18	0.0385	s
(141)	18.75	0.220	0.0505	s	{(115)	23.0	0.235	0.0495	f
(321)	22.4	0.20	0.0425	m	{(11 $\bar{5}$)	"	0.185	0.0385	f
(251)	33.6	0.17	0.029	w	{(313)	25.8	0.23	0.0455	f
(341)	34.4	0.165	0.0285	w	{(31 $\bar{3}$)	"	0.165	0.0325	w
(061)	36.8	0.16	0.0265	f	{(215)	28.8	0.215	0.0405	m
(161)	38.8	0.16	0.0255	f	{(21 $\bar{5}$)	"	0.155	0.029	ms
(512)	53.2	0.25	0.0345	f	(3 $\bar{2}$ 3)	"	0.34	0.0635	w
(532)	61.2	0.24	0.0305	f	{(314)	31.4	0.215	0.038	ms
{(013)	8.20	0.365	0.1275	f	{(31 $\bar{4}$)	"	0.145	0.0255	ms
{(01 $\bar{3}$)	"	0.33	0.116	mw	{(116)	31.8	0.205	0.0365	ms
{(210)	8.81	0.37	0.124	w	{(11 $\bar{6}$)	"	0.155	0.0275	ms
{(210)	"	0.305	0.103	m	{(411)	33.0	0.205	0.036	f
{(211)	9.61	0.355	0.115	mw	{(41 $\bar{1}$)	"	0.14	0.0245	f
{(21 $\bar{1}$)	"	0.29	0.0935	m	(324)	34.4	0.305	0.0525	w
{(212)	12.01	0.325	0.0935	w	{(126)	34.8	0.355	0.060	f
{(21 $\bar{2}$)	"	0.255	0.0735	mw	{(12 $\bar{6}$)	"	0.315	0.0535	f
{(014)	13.40	0.285	0.077	w	(421)	36.0	0.30	0.050	f
{(01 $\bar{4}$)	"	0.25	0.0675	w	(217)	37.6	0.175	0.029	mw
{(114)	15.75	0.28	0.070	mw	(315)	38.6	0.20	0.032	f
{(11 $\bar{4}$)	"	0.225	0.0565	vs	{(413)	39.4	0.195	0.0315	mw
{(213)	16.01	0.285	0.071	mw	{(41 $\bar{3}$)	"	0.125	0.020	f
{(21 $\bar{3}$)	"	0.215	0.0535	s	{(325)	41.6	0.345	0.0535	w
{(310)	18.55	0.26	0.0605	mw	{(32 $\bar{5}$)	"	0.275	0.043	mw
{(310)	"	0.205	0.0475	ms					

TABLE 1

Continued

hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.	hkl	$\frac{b^2}{d^2}$	$\sin\theta$	$\frac{n\lambda}{2b}$	Estim. Int.
$\begin{Bmatrix} (423) \\ (\bar{4}2\bar{3}) \end{Bmatrix}$	42.4 ,,	0.345 0.275	0.053 0.042	f f	$\begin{Bmatrix} (\bar{5}30) \\ (523) \end{Bmatrix}$	57.8 60.0	0.365 0.29	0.048 0.0375	w f
$\begin{Bmatrix} (027) \\ (02\bar{7}) \end{Bmatrix}$	43.2 ,,	0.32 0.285	0.049 0.0435	w mw	$\begin{Bmatrix} (\bar{5}2\bar{3}) \\ (327) \end{Bmatrix}$	,, 60.8	0.225 0.29	0.029 0.037	f f
(414)	45.0	0.185	0.028	f	$\begin{Bmatrix} (\bar{3}2\bar{7}) \\ (\bar{5}3\bar{2}) \end{Bmatrix}$	,, 61.0	0.225 0.355	0.029 0.0455	w w
$\begin{Bmatrix} (127) \\ (\bar{1}2\bar{7}) \end{Bmatrix}$	45.2 ,,	0.32 0.275	0.0475 0.0405	w w	$\begin{Bmatrix} (524) \\ (\bar{5}2\bar{4}) \end{Bmatrix}$	65.6 ,,	0.28 0.215	0.0345 0.0265	f f
(316)	47.4	0.18	0.025	w	$\begin{Bmatrix} (534) \\ (\bar{5}3\bar{4}) \end{Bmatrix}$	70.6 ,,	0.39 0.325	0.0465 0.0385	f w
(510)	49.8	0.175	0.0245	mw	$\begin{Bmatrix} (129) \\ (\bar{1}2\bar{9}) \end{Bmatrix}$	70.8 ,,	0.26 0.215	0.031 0.0255	f f
$\begin{Bmatrix} (227) \\ (\bar{2}2\bar{7}) \end{Bmatrix}$	51.0 ,,	0.305 0.25	0.043 0.035	f f	$\begin{Bmatrix} (525) \\ (\bar{5}2\bar{5}) \end{Bmatrix}$	72.8 ,,	0.265 0.20	0.031 0.023	f f
(415)	52.2	0.175	0.0245	w	$\begin{Bmatrix} (631) \\ (\bar{6}3\bar{1}) \end{Bmatrix}$	80.1 ,,	0.365 0.305	0.041 0.034	w w
(512)	53.0	0.17	0.0235	w	$\begin{Bmatrix} (536) \\ (\bar{5}3\bar{6}) \end{Bmatrix}$	86.6 ,,	0.36 0.29	0.0385 0.031	f f
$\begin{Bmatrix} (521) \\ (\bar{5}2\bar{1}) \end{Bmatrix}$	53.6 ,,	0.30 0.24	0.041 0.033	f f	(721)	100.4	0.23	0.023	f
(118)	54.2	0.16	0.022	f					
$\begin{Bmatrix} (522) \\ (\bar{5}2\bar{2}) \end{Bmatrix}$	56.0 ,,	0.30 0.235	0.040 0.0315	f f					
$\begin{Bmatrix} (128) \\ (\bar{1}2\bar{8}) \end{Bmatrix}$	57.2 ,,	0.285 0.24	0.038 0.032	w w					

Note: In this Table vs, s, ms, m, mw, w and f represent very strong, strong, medium strong, medium, medium weak, weak and faint.

The dimensions of the unit cell found from the spectrometric measurements are:

$$a = 5.47, b = 7.64, \text{ and } c = 8.54 \text{ \AA.},$$

the axial ratio being thus $a:b:c = 0.716:1:1.118$. The number of chemical molecules CSN_2H_4 in the unit cell is four, and followingly the calculated density is 1.408. These values of the axial ratio and the density are in good agreement with the above-mentioned values obtained by other means than X-rays. In Table 2 are shown the results of the measurements with the ionization spectrometer.

TABLE 2.
X-ray Spectrometric Data.

hkl	Spacing		Comparative Intensities of Reflection							
	Calc.	Obs.	I	II	III	IV	V	VI	VII	VIII
(100)	5.48	5.48	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 60 \\ (55) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 7 \\ (8.6) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (2.1) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (2.9) \end{Bmatrix}$
(010)	7.65	7.64	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 200 \\ (274) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (2.3) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 5.2 \\ (5.4) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 2 \\ (3.2) \end{Bmatrix}$
(001)	8.54	8.54	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 220 \\ (280) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 22 \\ (29) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 31 \\ (36) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 13 \\ (18) \end{Bmatrix}$
(021)	3.49	3.48	$\begin{Bmatrix} 80 \\ (90) \end{Bmatrix}$	$\begin{Bmatrix} 16 \\ (22) \end{Bmatrix}$						
(011)	5.70	5.70	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 80 \\ (89) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 16 \\ (18) \end{Bmatrix}$				
(012)	3.73	3.73	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 40 \\ (24) \end{Bmatrix}$						
(201)	2.61	2.61	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 16 \\ (13) \end{Bmatrix}$						
(101)	4.61	4.60	$\begin{Bmatrix} 45 \\ (83) \end{Bmatrix}$	$\begin{Bmatrix} 9 \\ (14) \end{Bmatrix}$	$\begin{Bmatrix} 13 \\ (14) \end{Bmatrix}$	$\begin{Bmatrix} 20 \\ (11) \end{Bmatrix}$				
(102)	3.37	3.37	$\begin{Bmatrix} 0 \\ (0) \end{Bmatrix}$	$\begin{Bmatrix} 18 \\ (19) \end{Bmatrix}$						
(210)	2.58	2.58	$\begin{Bmatrix} 0 \\ (0.9) \end{Bmatrix}$	$\begin{Bmatrix} 10 \\ (9) \end{Bmatrix}$	$\begin{Bmatrix} 1 \\ (4) \end{Bmatrix}$					
(110)	4.45	4.46	$\begin{Bmatrix} 170 \\ (183) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (3.3) \end{Bmatrix}$	$\begin{Bmatrix} 0 \\ (2.7) \end{Bmatrix}$	$\begin{Bmatrix} 10 \\ (8.5) \end{Bmatrix}$				
(120)	3.14	3.13	$\begin{Bmatrix} 210 \\ (141) \end{Bmatrix}$	$\begin{Bmatrix} 15 \\ (21) \end{Bmatrix}$	$\begin{Bmatrix} 3 \\ (7) \end{Bmatrix}$					

The Space Group. On inspecting the data in Tables 1 and 2, various reflecting planes were found to show the following characteristics:

(1) In the first order reflection from pyramidal planes, there are all kinds of combinations of even and odd integers for their indices h , k and l .

(2) No odd order reflection is observed from any of the planes (100), (010) and (001).

(3) All prismatic planes are divided into two groups, (A) and (B):

(A) The prismatic planes, having the indices of (zero, even, odd), (odd, zero, odd), (odd, odd, zero), (odd, even, zero) or (even, odd, zero), show odd order reflections; e. g. (021), (061), (027), (101), (301), (110), (310), (510), (120), (210).

(B) Those, having the indices of (zero, odd, odd), (zero, odd, even), (even, zero, odd) or (odd, zero, even), show no odd order reflection; e. g. (011), (012), (201), (102).

From (1) it is obvious that the corresponding space group should be one of those that are based upon the simple orthorhombic translation group

Γ_0 ; viz. one of the space groups C_{2v}^1 to C_{2v}^{10} , V^1 to V^4 , and V_h^1 to V_h^{16} .⁽¹⁾ While, in the general criteria of the space groups, the conditions for the presence of certain reflection may not fully correspond to the experimental data, all the requirements for the absence should be necessarily satisfied, or, in the present case, any space group that is in conflict with the evidence (3A) can never be chosen as the corresponding one. Accordingly (3A) was first used to sort out the possible space groups, and these were found to be C_{2v}^1 , C_{2v}^2 , C_{2v}^4 , C_{2v}^7 , C_{2v}^9 , V^1 , V^2 , V^3 , V^4 , V_h^1 , V_h^6 , V_h^{13} and V_h^{16} . Of these space groups C_{2v}^9 and V_h^{16} are fitted exactly to all the conditions (1) to (3), whereas the rest may show odd order reflections from more sorts of planes than those in (3A). As already noticed, it may also be possible for any of the above space groups other than C_{2v}^9 and V_h^{16} to account for the observed nonpresence of the predicted reflections, but, to do this, atoms should be arranged at some special positions. In the present case, however, this is very improbable, if not impossible, and it seems unnecessary to treat such space groups further. As to C_{2v}^9 and V_h^{16} , it is impossible so far to distinguish one from the other, the general criteria coming to the same.⁽²⁾

The Atomic Arrangement. In case that the corresponding space group is C_{2v}^9 ,⁽³⁾ the crystals of thiourea must have hemimorphic polarity along the c -axis, whose existence, however, has never been proved. On the other hand, since the space group V_h^{16} is in accord with the observed symmetry, it may be regarded as the correct one, if there is found an arrangement of atoms which accounts for the observed data respecting the comparative intensities of reflection. The space group V_h^{16} has the following equivalent positions⁽⁴⁾ in all:

Four-fold positions

$$(a) \quad 0 \frac{1}{4} \frac{1}{4}; \quad 0 \frac{1}{4} \frac{3}{4}; \quad \frac{1}{4} \frac{3}{4} \frac{3}{4}; \quad \frac{1}{2} \frac{3}{4} \frac{1}{4}.$$

$$(b) \quad \frac{1}{2} \frac{1}{4} \frac{1}{4}; \quad \frac{1}{2} \frac{1}{4} \frac{3}{4}; \quad 0 \frac{3}{4} \frac{3}{4}; \quad 0 \frac{3}{4} \frac{1}{4}.$$

$$(c) \quad u \ v \ 0; \quad -u, \frac{1}{2} - v, \frac{1}{2}; \quad \frac{1}{2} - u, \frac{1}{2} + v, 0; \quad \frac{1}{2} + u, -v, \frac{1}{2}.$$

(1) See for instance R.W.G. Wyckoff, *Am. J. Sci.* 9 (1925), 145, or H. Mark, "Die Verwendung der Röntgenstrahlen in Chemie und Technik," (1926), 387.

(2) Very recently Professor S. Nishikawa and Mr. K. Matukawa (*Proc. Imp. Acad. (Japan)*, 4 (1928), March) have found an effect of hemihedry of zincblende upon X-ray reflection, but it is not yet applicable to the present case.

(3) As the general equivalent positions are four-fold here and the unit cell contains four chemical molecules CSN_2H_4 , it can be inferred that the shape of the molecule is not restricted by any condition of symmetry, the parameters to be determined being more than ten.

(4) See for instance R.W.G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," (1922), or H. Mark, loc. cit., Table 52.

Eight-fold positions

$$(d) \quad x y z; \quad -x, \frac{1}{2} - y, \frac{1}{2} + z; \quad \frac{1}{2} - x, \frac{1}{2} + y, -z; \quad \frac{1}{2} + x, -y, \frac{1}{2} - z; \\ -x, \frac{1}{2} - y, \frac{1}{2} - z; \quad x, y, -z; \quad \frac{1}{2} + x, -y, \frac{1}{2} + z; \quad \frac{1}{2} - x, \frac{1}{2} + y, z.$$

The positions (a) and (b) coincide with the centres of symmetry, and (c) are in the planes of symmetry. There are four molecules in the unit cell, so that four atoms of carbon, four atoms of sulphur, eight atoms of nitrogen and sixteen atoms of hydrogen should be arranged in it. As is generally the case for organic crystals, it is highly probable that the crystals of thiourea will form a molecular lattice. If so, the 4C atoms or the 4S atoms cannot be placed in the positions (a) or (b); for no atomic arrangement can give a centre of symmetry to a single molecule CSN_2H_4 . The observed comparative intensities of reflection from principal planes also favour to exclude such possibilities. Accordingly the atoms of carbon and sulphur should be arranged in the planes of symmetry, their positions being (c) with respective set of parameter values. That the nitrogen atoms should be arranged in the general equivalent positions (d) comes out directly from the inspection of the distribution of intensities of reflection among various orders from (001) plane. Sixteen hydrogen atoms will be divided into two groups, each being situated at (d).

In determining the arrangement, the atoms of hydrogen may be neglected as usually done, then there is only one parameter z_N for the nitrogen atoms in the direction of the c -axis. A value about 0.144 for z_N was found to account well for the observed distribution of the intensities of reflection among various orders from (001). With this value the distance between the two nitrogen atoms in a molecule becomes about 2.46 Å. As this seemed not in the least inadequate, it was further attempted to determine the values of the remaining parameters, which, being as many as six, will hardly be evaluated without some assumption. Therefore, it was assumed that one carbon atom and two nitrogen atoms form an isosceles triangle NCN (Fig. 1), the distance between the two N atoms being the above value 2.46 Å., and that between the carbon atom and one of the nitrogen atoms being very nearly 1.44–1.48 Å. as found in the case of hexamethylene tetramine.⁽¹⁾ Upon this a trial survey was made, and it was

(1) R.G. Dickinson and A.L. Raymond, *J. Am. Chem. Soc.*, **45** (1923), 22; H.W. Gonell and H. Mark, *Z. physik. Chem.*, **107** (1923), 181.

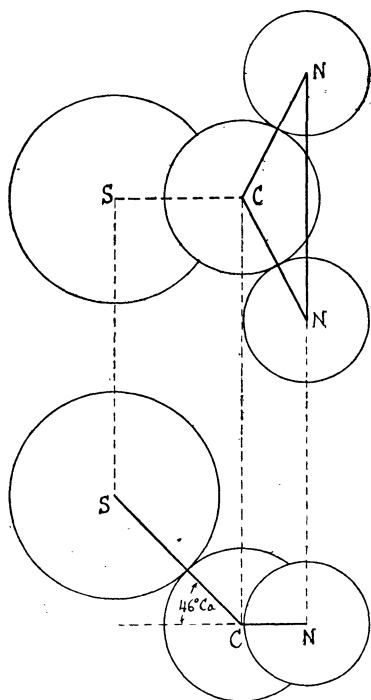


Fig. 1.

Discussion of the Structure. With the above parameter values the C, S and 2N atoms in a molecule do not lie in the same plane, but the direction from the carbon to the sulphur atom makes an angle of about 46° to the plane NCN. The interatomic distance between sulphur and carbon is $1.81\text{\AA}$., which is in good agreement with the sum of radii of the neutral atoms for S and C, $1.04 + 0.77 = 1.81\text{\AA}$. according to Wyckoff⁽¹⁾ or Goldschmidt.⁽²⁾ Each one of the

found that a set of parameter values accounted for the comparative intensities given in Table 2. These values are: $u_C = 0.186$, $v_C = 0.144$ for the carbon atoms; $u_S = -0.095$, $v_S = 0.270$ for the sulphur atoms; and $x_N = 0.300$, $y_N = 0.164$, $z_N = 0.144$ for the nitrogen atoms. In Table 2, the figures without brackets are the intensities observed and those within brackets right under them are the intensities calculated by a formula $\left(\frac{d}{n}\right)^{2.35} |S|$, where d denotes the spacing, n the order of reflection and $|S|$ the absolute value of structure amplitude, the reflecting powers of the atoms being roughly assumed to be proportional to their atomic numbers.

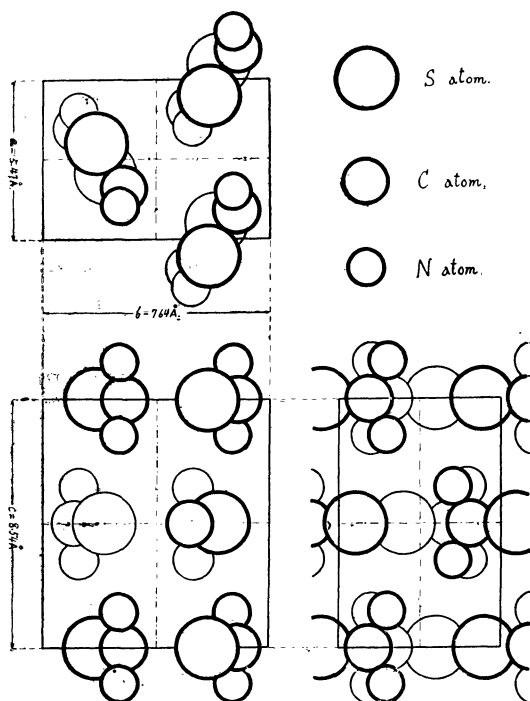


Fig. 2.

(1) R.W.G. Wyckoff, *Proc. Nat. Acad. Sci.*, 9 (1923), 33.

(2) V.M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo. I. Matemat.-Natur. Klasse*, (1926), No. 2.

nitrogen atoms is at a distance of $1.39 \text{ \AA}$. from the carbon atom, which is somewhat less than the value in hexamethylene tetramine or the sum of radii of the neutral carbon and nitrogen atoms $0.77 + 0.71 = 1.48 \text{ \AA}$. according to Goldschmidt, but is concordant with the sum $0.77 + 0.63 = 1.40 \text{ \AA}$. given by Wyckoff. To complete the crystal structure of thiourea, the positions of the hydrogen atoms hitherto neglected should be considered, and, as a matter of fact, there is a vacant place left for them to be so arranged that the molecular structure may correspond to the usual chemical formula $\text{SC}(\text{NH}_2)_2$. As for the connection between neighbouring molecules, it is closer in the zx -plane than in the direction of the y -axis, which corresponds to the existence of perfect cleavage on (010) plane. Besides, it may also be noted that the largest spacing was found in the direction of the c -axis to be $d_{(001)} = 8.54 \text{ \AA}$., and, as already described, there was actually observed a case in which thiourea crystallized in plates parallel to (001)⁽¹⁾. The arrangement of atoms in the crystal is shown in Fig. 2.

According to Hark and Weissenberg, urea crystallizes in the space group V_a^3 of the tetragonal scalenohedral class, the unit cell being of the dimensions $a = 5.63$ and $c = 4.70 \text{ \AA}$. The molecule is tied up spatially in one group, is flat on neglect of H atoms and has the proper symmetry of C_2^v . Such a structure of urea seemingly bears no close relation to that of thiourea. This may correspond to the separate crystallization from the aqueous solution containing these compounds. The unit cell of the former contains two chemical molecules CON_2H_4 , and the line joining the two nitrogen atoms of a molecule stands perpendicular to that of the other, while the unit cell of the latter contains four molecules CSN_2H_4 , and the corresponding lines for every pair of nitrogen atoms are all parallel to each other. The distance between the two N atoms in the molecule is about $2 \text{ \AA}$. for urea, and $2.46 \text{ \AA}$. for thiourea. As to the molecular symmetry, C_s of the latter is lower than C_2^v of the former. In spite of these differences, however, they are not quite unrelated to each other; for it is also possible to change the crystal structure of thiourea into that of urea by making every molecule flat in the zx -plane and giving it a small amount of translation and a rotation through half a right angle about the axis C-S.

In conclusion, the authors wish to express their best thanks to Professor S. Nishikawa for his kind interest and encouragement during the work.

(1) cf. H. Mark, loc. cit., 340.

Summary.

Using the Laue photographic and X-ray spectrometric methods the crystal structure of thiourea was investigated. The unit of structure built upon the simple orthorhombic translation group Γ_0 , is of the dimensions $a = 5.47$, $b = 7.64$ and $c = 8.54$ Å., and contains four chemical molecules of CSN_2H_4 . Thus the density is 1.408. The plausible space group being V_h^{16} , a possible atomic arrangement, neglecting H atoms, was found to be as follows:

$$4\text{C} \left\{ u, v, 0; \quad -u, \frac{1}{2} - v, \frac{1}{2}; \quad \frac{1}{2} - u, \frac{1}{2} + v, 0; \quad \frac{1}{2} + u, -v, \frac{1}{2} \right\}$$

with $u = 0.186$, $v = 0.144$;

$$4\text{S} \left\{ u, v, 0; \quad -u, \frac{1}{2} - v, \frac{1}{2}; \quad \frac{1}{2} - u, \frac{1}{2} + v, 0; \quad \frac{1}{2} + u, -v, \frac{1}{2} \right\}$$

with $u = -0.095$, $v = 0.270$; and

$$8\text{N} \left\{ \begin{array}{l} x, y, z; \quad -x, \frac{1}{2} - y, \frac{1}{2} + z; \quad \frac{1}{2} - x, \frac{1}{2} + y, -z; \quad \frac{1}{2} + x, -y, \frac{1}{2} - z; \\ -x, \frac{1}{2} - y, \frac{1}{2} - z; \quad x, y, -z; \quad \frac{1}{2} + x, -y, \frac{1}{2} + z; \quad \frac{1}{2} - x, \frac{1}{2} + y, z \end{array} \right\}$$

with $x = 0.300$, $y = 0.164$ and $z = 0.144$. The molecule has the symmetry of C_s , i.e. it has one plane of symmetry in it. In such a model, the distance C-S is 1.81 Å., and that C-N is 1.39 Å. Discussion was also made upon its crystalline and molecular structures in comparison with those of urea.

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ON THE OXIDATION OF FERROUS HYDROXIDE IN SODIUM 137 HYDROXIDE SOLUTION BY MEANS OF AIR.

By Susumu MIYAMOTO.

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The principal purpose of the previous study⁽¹⁾ on the oxidation of ferrous hydroxide by means of air was to know the effect of sodium hydroxide on the reaction, and the oxidation velocity in the first stage was only studied. The present research was carried out to study the reaction under almost the same conditions more completely.

Experimental. The experimental procedure was quite the same as that described in the previous paper,⁽¹⁾ only a large test-tube (diameter=3 cm.) was used for the reacting vessel as in the case of the oxidation of sodium sulphite⁽²⁾ or stannous hydroxide,⁽³⁾ instead of an Erlenmeyer flask (100 cc.), which was used in the previous study.

After t -minutes the air current was stopped and the total quantity of ferrous and ferric hydroxide was dissolved in sulphuric acid in the atmosphere of carbon dioxide by Jahoda's method,⁽⁴⁾ and the amount of ferrous sulphate thus formed was titrated with 0.1000 normal potassium permanganate solution, the volume of which is given as v in the following tables. The values of k were obtained by $k = \frac{1}{t} (v_0 - v)$, v_0 being the value of v at $t=0$, and the values of $v_{calc.}$ were calculated by $v_{calc.} = v_0 - k t$, using the mean value of k .

TABLE 1.
Temp.=20° C. Velocity of air=7.78 litres per hour.

C _{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0470	0	11.87	—	—
	10	9.10	9.00	0.277
	15	7.36	7.56	0.301
	25	4.65	4.69	0.289
	0	24.00	—	—
	15	19.74	19.69	0.284
	30	16.04	15.39	0.265
	50	9.69	9.65	0.286
	0	11.47	—	—
	10	8.44	8.60	0.303
	20	5.69	5.73	0.289
	30	2.73	2.86	0.291
Mean : 0.287				

(1) S. Miyamoto, this journal, 2 (1927), 40.

(2) Ibid., 2 (1927), 74.

(3) Ibid., 2 (1927), 155.

(4) Lunge-Berl, "Chemisch-technische Untersuchungsmethoden", 7. Aufl., 2. Bd., S. 135.

TABLE 1. (Continued.)

C_{NaOH} normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k
0.1700	0	23.75	—	—
	15	19.62	19.55	0.276
	30	15.46	15.35	0.276
	55	8.07	8.35	0.285
	0	11.41	—	—
	10	8.67	8.61	0.274
	20	5.80	5.81	0.281
	30	2.81	3.01	0.287
	Mean : 0.280			
0.5494	0	11.71	—	—
	10	9.39	9.40	0.232
	20	7.03	7.09	0.234
	30	4.77	4.78	0.231
	0	12.35	—	—
	10	10.08	10.04	0.227
	20	7.71	7.73	0.232
	30	5.49	5.42	0.229
	Mean : 0.231			
1.130	0	11.59	—	—
	10	9.97	9.89	0.162
	20	8.19	8.19	0.170
	40	4.71	4.79	0.172
	0	12.35	—	—
	10	10.67	10.65	0.168
	20	8.92	8.95	0.172
	40	5.22	5.55	0.178
	Mean : 0.170			
1.670	0	11.49	—	—
	15	9.78	9.61	0.114
	30	7.85	7.74	0.121
	55	4.23	4.61	0.132
	0	12.31	—	—
	15	10.42	10.43	0.126
	30	8.53	8.56	0.126
	55	5.09	5.43	0.131
	Mean : 0.125			
2.260	0	11.49	—	—
	15	10.19	10.06	0.0867
	30	8.75	8.62	0.0913
	60	5.44	5.76	0.1008
	0	11.49	—	—
	15	10.07	10.06	0.0947
	30	8.55	8.62	0.0980
	60	5.41	5.76	0.1013
	Mean : 0.0955			

As is seen in Table 1, the oxidation velocity of ferrous hydroxide is independent of the amount of ferrous hydroxide present in the reacting vessel, and the values of the velocity constants are almost the same as those of the velocity constants of the oxidation of sodium sulphite⁽¹⁾ or stannous hydroxide⁽²⁾ in sodium hydroxide solution under the same conditions. The coincidence of the values of their velocity constants is shown in Table 2 and graphically in Fig. 1. It can be considered, from the above results, that the oxidation velocity of ferrous hydroxide under the conditions of the author's measurements is no other than the dissolution velocity of oxygen when air was passed into sodium hydroxide solution.

Strictly speaking, the presence of solid phase in the solution will have some effect on the dissolution velocity of oxygen, but the experimental error of the present experiment will be too great to discuss it precisely.

TABLE 2.
Temp. = 20° C.

C_{NaOH} Normal	k			$k_{\text{calc.}}$ (=0.278-0.0942 C_{NaOH})
	Na_2SO_3	$\text{Sn}(\text{OH})_2$	$\text{Fe}(\text{OH})_2$	
0	0.330	—	—	—
0.02888	0.298	—	—	0.275
0.0470	—	—	0.287	0.274
0.05173	0.276	—	—	0.273
0.1700	—	—	0.280	0.262
0.1706	—	0.257	—	0.262
0.1810	0.265	—	—	0.261
0.2204	—	0.259	—	0.258
0.3252	—	0.246	—	0.248
0.5173	0.231	—	—	0.229
0.5494	—	—	0.231	0.226
0.5500	—	0.215	—	0.226
0.7219	0.213	—	—	0.210
1.1011	0.169	—	—	0.174
1.130	—	0.168	0.170	0.172
1.670	—	—	0.125	0.121
1.704	—	0.126	—	0.117
1.810	0.0989	—	—	0.107
2.260	—	—	0.0955	—
2.312	—	0.0998	—	—

(1) Loc. cit.

(2) Loc. cit.

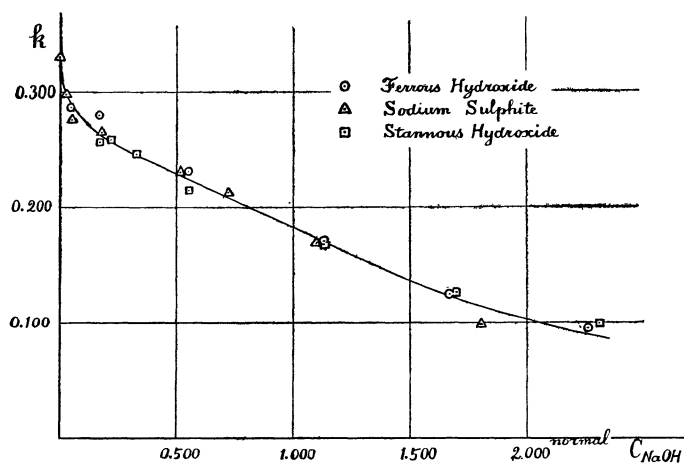


Fig. 1.

TABLE 3.

Air=7.78 litres per hour.

Temp.	C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
30° C.	0.0470	0	13.27	—	—
		10	10.39	10.31	0.288
		20	7.22	7.35	0.303
		30	4.56	4.39	0.290
		0	14.37	—	—
		10	8.36	8.41	0.301
	0.5494	15	6.89	6.93	0.299
		25	4.01	3.97	0.294
		Mean : 0.296			
		0	13.25	—	—
		10	10.70	10.87	0.255
		20	8.40	8.49	0.243
		35	5.04	4.92	0.235
	0.0470	0	11.23	—	—
		10	8.78	8.85	0.245
		20	6.57	6.47	0.233
		30	4.67	4.09	0.219
		Mean : 0.238			
		0	13.15	—	—
40° C.	0.0470	10	10.08	10.12	0.307
		20	7.24	7.09	0.296
		30	4.28	4.06	0.296
		0	11.16	—	—
		10	8.16	8.13	0.300
		15	6.55	6.61	0.307
	0.5494	25	3.41	3.58	0.310
		Mean : 0.303			

TABLE 3. (Continued.)

Temp.	C_{NaOH} Normal	t min.	v c.c.	$v_{\text{calc.}}$ c.c.	k
40° C.	0.5494	0	12.96	—	—
		10	10.25	10.29	0.271
		20	7.59	7.62	0.269
		30	5.20	4.95	0.259
		0	12.87	—	—
		10	10.15	10.20	0.272
		20	7.46	7.53	0.271
		30	5.06	4.86	0.260
		Mean : 0.267			

The Effect of Temperature. The results of the measurements at 30° C. and 40° C. are given in Table 3. The effect of temperature was small, as can be expected.

$$\frac{k_{30^\circ}}{k_{20^\circ}} = \frac{0.296}{0.287} = 1.03, \quad \frac{k_{40^\circ}}{k_{30^\circ}} = \frac{0.303}{0.296} = 1.03$$

when $C_{\text{NaOH}} = 0.0470$ normal

$$\frac{k_{30^\circ}}{k_{20^\circ}} = \frac{0.238}{0.231} = 1.03, \quad \frac{k_{40^\circ}}{k_{30^\circ}} = \frac{0.267}{0.238} = 1.12$$

when $C_{\text{NaOH}} = 0.5494$ normal

Summary.

(1) The velocity of the oxidation of ferrous hydroxide by means of air was studied. The rate of the oxidation was independent of the quantity of ferrous hydroxide present in the reacting vessel, and the values of the velocity constants were almost the same as those of the velocity constants of the oxidation of sodium sulphite or stannous hydroxide under the same conditions.

(2) The effect of temperature was small.

(3) Sodium hydroxide decreases the velocity of the oxidation, the mechanism of which will be explained by the considerations that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen under the conditions above described, and that sodium hydroxide decreases the dissolution velocity of oxygen into the solution.

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BEMERKUNGEN UEBER DIE ZUSTANDSGLEICHUNGEN DER ADSORBIERTEN PHASEN. II.

Von **Bun-ichi TAMAMUSHI.**

Eingegangen am 26. April 1928. Ausgegeben am 28. Juni 1928.

Die Zustandsgleichung der adsorbierten Phase

$$P_s(A-\beta) = iRT \dots \dots \dots (1)$$

ist von Rideal⁽¹⁾ für Lösungen gesättigter homologer Fettsäuren eingehend untersucht worden, wobei P_s der Grenzflächen-Druck, A die molare Oberfläche des Adsorbens, β eine Flächenkorrektur und $1/i$ die laterale Kohäsion der adsorbierten Moleküle bedeutet. Die Notwendigkeit, die Anziehungskraft zwischen adsorbierten Molekülen zu berücksichtigen wurde auch von Frumkin,⁽²⁾ insbesondere für höhere Säuren betont. Denn das mechanische Verhalten der dünnen Schichten dieser Säuren, dass sie nämlich eine typische Kondensations-Erscheinung bilden, kann so verstanden werden, dass im Vordergrund der Erscheinung diese Anziehungskraft voraussetzt wird. Im folgenden sollen die Bemerkungen über die Zustandsgleichungen, und zwar besonders über den Koeffizienten i , die ich in meinem vorigen Bericht⁽³⁾ gemacht habe, ergänzt werden. Da unsere Kenntnis von der Struktur der adsorbierten Schichten noch nicht hinreicht, sind die folgenden Darlegungen nur erst annähernd durchgeführt worden.

Die elektrostatische Deutung der van der Waalschen Kraft der Gasmoleküle verdanken wir den Arbeiten von Debye,⁽⁴⁾ Keesom,⁽⁵⁾ sowie von Falkenhagen,⁽⁶⁾ wobei solche Moleküle in Frage kommen, die im Zeitmittel alle mögliche gegenseitige Orientierungen annehmen können. Im Falle der dünnen Schichten der gesättigten Fettsäuren dagegen, besonders im Gültigkeitsbereich der Ridealschen Gleichung, handelt es sich um Moleküle, die der Grenzfläche in bestimmter Orientierung angelagert sind. Dabei werden nach der Langmuir-Adamsschen Vorstellung parallel gerichtete Moleküle sowie unimolekuläre Charakter der Schichten angenommen. Aber über die gegenseitige Orientierung der Dipole, die in diesen Kettenmolekülen sowohl starr wie induziert vorhanden sein könnten, wissen wir fast gar nichts Bestimmtes. Höchstens könnte nach den Frumkinschen Versuchen⁽⁷⁾

(1) Rideal und Schonfield, *Proc. Roy. Soc., A*, **109** (1925), 57; **110** (1926), 167.

(2) A. Frumkin, *Z. physik. Chem.*, **116** (1925), 466.

(3) B. Tamamushi, diese Zeitschr., **2** (1927), 299.

(4) P. Debye, *Physik. Z.*, **21** (1920), 1801.

(5) W. H. Keesom, *Physik. Z.*, **22** (1921), 129; **23** (1922), 225.

(6) H. Falkenhagen, *Physik. Z.*, **23** (1922), 87.

(7) A. Frumkin, *Z. physik. Chem.*, **111** (1924), 206.

vermutet werden, dass auch die Dipolaxen parallel zu einander gerichtet sind, denn die Grenzfläche sich positiv laden lässt. Im Grunde haben ja doch die Dipole die Neigung, sich im Zustande des minimalen Potentials zu orientieren, obwohl die thermische Bewegung stets hemmend wirkt. Und solange der Abstand beider Dipolzentren noch verhältnismässig grösser bleibt als die Dipollänge, dürften wir erwarten, dass zwischen ihnen eine Anziehungskraft besteht. Diese potentiale Energie lässt sich folgendermassen ausdrücken⁽¹⁾

$$U = - \frac{\mu^2}{r^3} f(\xi_a, \varepsilon_0), \dots \dots \dots (2)$$

wobei μ das Dipolmoment des starren Dipols, r den Abstand beider Dipolzentren und $f(\xi_a, \varepsilon_0)$ eine Funktion, die die Abhängigkeit von Polarisierung sowie von Temperatur darstellt.

Der Polarisations-Effekt, der im Dielektrikum eigentlich vorhanden sein müsste, sei hier Einfachheits halber vernachlässigt. Über den Temperatur-Effekt sei nur bemerkt, dass die mittlere Energie nach dem Maxwell-Boltzmannschen Prinzip zu bestimmen ist, nämlich

$$\bar{U} = \frac{\int U \cdot e^{-\frac{U}{kT}} d\Omega}{\int e^{-\frac{U}{kT}} d\Omega}, \dots \dots \dots (3)$$

wo Ω den räumlichen Winkel, k die Boltzmannsche Konstante und T die absolute Temperatur bedeutet. Diese Energie ist diejenige, die wir schon oben in der Zustandsgleichung neben der kinetischen berücksichtigen mussten.

Massgebend ist der Koeffizient μ^2/r^3 , der sich mit i in Gleichung (1) folgendermassen verknüpfen wird.

(1) Diese Energie ist die augenblickliche gegenseitige Energie, die bei der Zeitmittelbildung nicht wegfällt. Die mittlere Energie der starren Dipole im Gaszustand, die alle mögliche Orientierungen annehmen können, beträgt dagegen, $\bar{U} = - \frac{2}{3} \frac{\mu^4}{r^6} \frac{1}{kT} - \frac{385}{225} \frac{\mu^6}{r^{12}} \left(\frac{1}{kT} \right)^2 \dots$ Eine analoge Formel ist von Lorenz-Lande und E. Jacket, vor kurzem von O. Blüh für die Adsorptionsenergie gegeben worden. Bei ihnen wird aber der Dipol von seinem eigenen Spiegelbild angezogen, hier dagegen der Effekt des benachbarten Dipols betrachtet. Zum Unterschied habe ich deshalb die Richtungslinie statt mit h mit r bezeichnet. Die Spiegelbild-Energie der Lorenz-Landeschen Auffassung würde in unserem Fall, wo es sich um parallel gerichtete kettenartige Moleküle an der Wasser-Luft-Grenzfläche handelt, verhältnismässig unbedeutend sein. In welchem Verhältnis allgemein die Attraktion von Adsorbentien und die Kohäsion der adsorbierten Moleküle zu einander stehen, wird noch in einem anderen Bericht behandelt. Verg. Lorenz und Lande, *Z. anorg. allgem. Chem.*, **125** (1922), 47; E. Jacket, *Fortschr. Physik. u. physik. Chem.*, **18** (1925); O. Blüh, *Z. Physik.* **43** (1927), 575.

$$1-i = \frac{\mu^2/r^3}{kT}, \dots\dots\dots(4)$$

worin k die Boltzmannsche Konstante bedeutet. Nun ist $1-i$ oder η , das das Verhältnis zwischen elektrostatischer und kinetischer Energie darstellt, nach der Ridealschen Berechnung für verschiedene Fettsäuren bekannt. Da die Versuchstemperatur $18\sim 20^\circ\text{C}$. war, sei kT einfach gleich 4×10^{-14} c.g.s. gesetzt. Falls uns der Abstand r bekannt ist, lässt sich also μ berechnen. Bei paralleler Orientierung der Moleküle könnte man r dadurch annähernd abschätzen, dass man es gleich $\sqrt{\frac{A}{N}}$ setzt, wobei A aus P_s und $P_s A/RT$ zu berechnen oder eventuell direkt messbar ist, und N die Avogadro'sche Konstante. Die Ergebnisse zeigt folgende Tabelle:

TABLE.

Substanz	Buttersäure	Valeriansäure	Capronsäure
Chem. Formel	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$
i	0.73	0.63	0.43
$\eta = 1-i$	0.27	0.37	0.57
P_s dyne/cm.	$10.6 \sim 31.4$	$11.0 \sim 33.6$	$9.2 \sim 34.3$
$r = \sqrt{A/N}$	6.5×10^{-8}	6.0×10^{-8}	5.6×10^{-8}
μ elektrost. Einheit	17×10^{-19}	18×10^{-19}	20×10^{-19}
Substanz	Caprylsäure	Caprinsäure	Laurinsäure
Chem. Formel	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
i	0.46	0.35	0.23
$\eta = 1-i$	0.54	0.65	0.77
P_s dyne/cm.	$11.0 \sim 27.0$	$14.9 \sim 24.7$	$10.2 \sim 19.8$
$r = \sqrt{A/N}$	5.5×10^{-8}	5.5×10^{-8}	5.5×10^{-8}
μ elektrost. Einheit	19×10^{-19}	21×10^{-19}	22×10^{-19}

Hierzu sei bemerkt, dass r aus den Werten von P_s und $P_s A/RT$ berechnet wurde, und zwar als Mittelwert im Bereich von P_s , $10\sim 35$ dyne/cm. bei den ersten drei niedrigen Körpern, und im Bereich von P_s , $10\sim 27$ dyne/cm. bei den höheren Körpern. Die Gleichung (1) ist von $P_s=10$ dyne/cm. ab für jeden Körper gültig und in den oben ausgewählten Temperaturen und Bereichen von P_s könnten sich die Schichten noch nicht in kondensiertem Zustand

befinden, sondern müssten gasförmig oder expandiert sein. Unter diesen Umständen ist es nicht unwahrscheinlich, dass der Molekularabstand durchschnittlich umso kleiner wird, je grösser die Molekularlänge bzw. die Kohäsion ist. Es ergibt sich daraus für das Dipolmoment fast ein konstanter Wert (20×10^{-19}), der von dem Molekulargewicht unabhängig zu sein scheint. Diese Schlussfolgerung wäre plausibel, da wir die polare Eigenschaft dieser Kettenmoleküle, unabhängig ihrer Molekularlänge, hauptsächlich der aktiven Gruppe COOH zuschreiben könnten. Müssten wir dabei den Temperatur- und Polarisations-Effekt berücksichtigen, so wäre der gesamte Einfluss nicht gross.⁽¹⁾ Aber bei dieser nur annähernd durchgeführten Berechnung, können wir natürlich nicht erwarten, damit das richtige Dipolmoment zu ermitteln.

Sollte einmal der Fall eintreten, dass die Moleküle an der Grenzfläche fest zusammen gedrängt sind („close packing“), dann würde die ganze Sachlage wohl eine andere sein. Die Kohäsion könnte dann wesentlich von verschiedenen Teilen des Moleküls abhängig werden, und der Wert des Dipolmoments wäre mit $30 \sim 90 \times 10^{-19}$ vergleichbar, die Born für flüssige Kristalle berechnet hat.⁽²⁾

Das besondere Interesse, das die Ridealsche Untersuchung für uns bietet, dürfte darin liegen, dass die isothermischen $P_s A/RT$, P_s -Kurven der homologen Fettsäuren den P_v/RT , P -Kurven eines gases (z. B. CO_2) bei verschiedenen Temperaturen ganz analog laufen. Es zeigt sich nämlich, dass sich der Zustand dieser dünnen Schichten mit der Zunahme des Molekulargewichts des adsorbierten Körpers vom gasförmigen zum expandierten sowie kondensierten Zustand verschiebt. Nach den Versuchen Adams⁽³⁾ ist uns auch bekannt, dass die P_s , A -Kurven irgendeiner höheren Säure und anderer Substanzen (z. B. Myristinsäure) bei verschiedenen Temperaturen der Schar der bekannten P , v -Kurven einer einheitlichen Substanz im kritischen Gebiete weit analog verlaufen. Nähere Untersuchungen in dieser Richtung wären erwünscht, um damit die Theorie des Zustands der dünnen Schichten genauer zu entwickeln.

Im folgenden seien mir noch kurze Bemerkungen über die Flächenkorrektur β gestattet. Die Ridealsche Gleichung erklärt den Zustand dünner Schichten, soweit der Grenzflächendruck genügend gross bleibt. Der Wert von β (pro. Molekül), der für jede der homologen gesättigten Fettsäuren recht konstant $24 \sim 25 \times 10^{-10} \text{ cm}^2$ erreicht wurde, entspricht freilich der minimalen Fläche, die die Gruppe CH_3 bei dichter Lagerung anzunehmen

(1) Verg. E. Jacket, loc. cit.

(2) M. Born, *Ann. Physik*, [4], 55 (1918), 1771.

(3) N. K. Adams, *Proc. Roy. Soc.*, [A], 101 (1922), 452 & 516; 103 (1923), 687.

und den Ergebnissen der Röntgenographischen Untersuchungen wohl vergleichbar ist. In gasförmigem oder expandiertem Zustand müsste, auch wenn die Moleküle sich dabei in paralleler Orientierung befinden könnten, der Wirkungsquerschnitt des Moleküls grösser sein als $25 \times 10^{-16} \text{ cm.}^2$, und zwar würde bei löslichen Molekülen, die in verdünntem Zustand leicht einen Gas-Film bilden können, das Flächenbedürfnis des Moleküls in der Grenzfläche nicht ganz eindeutig sein, weil ja dann die Wahrscheinlichkeit, dass die Moleküle aus ihrer bestimmten Orientierung herausfallen, zunimmt und sie sich eventuell flach an die Oberfläche legen können.⁽¹⁾ Diesem Zustand würde der etwas grössere Wert von β entsprechen, den Langmuir sowie Volmer aus der Szyszkowskischen Konstante B berechnet haben. Die mittleren Werte von A/N , die oben benutzt wurden, sind ebenfalls mit den Langmuir-Volmerschen Ergebnissen vergleichbar. Die Volmersche Gleichung $P_s(A-\beta) = RT^{(2)}$ hat also bei leicht löslichen Substanzen Giltigkeit, soweit die Dichte nicht zu gross ist (wir können dabei die Druckkorrektur vernachlässigen), wie Volmer selbst bemerkt hat. Aber die Forderung, dass β in der Volmerschen Gleichung das Zweifache der wirklichen Molekulfläche sein müsse, könnte keine wesentliche Bedeutung haben, soweit nichtkugelige Moleküle in Frage kommen.

März 1928.

Berlin, Deutschland.

(1) I. Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848.

(2) M. Volmer, *Z. physik. Chem.*, **115** (1925), 253.

THE INFLUENCE OF SALTS ON THE ISO-ELECTRIC BEHAVIOR OF THE PROTEIN.

By Kinsuke KONDO and Tsunetomo HAYASHI.

Received May 3, 1928. Published June 28, 1928.

Introduction. The point of maximum flocculation of such a difficult soluble protein as rice-glutelin or casein does not show the iso-electric point of the protein. We call this point an apparent iso-electric point.⁽³⁾ This apparent iso-electric point is movable according to the concentration and kind of salts in the buffer solution. This is caused by the fact that the protein in the salt solution is not able to behave as an iso-electric protein, because the addition of salt causes a change in the hydrogen ion activity of the solution, and the cations and anions, which are derived by the dissociation of the salt, force the protein molecule to ionize in the opposite charge and in a different degree. Hence, the protein molecule will be ionized

(3) K. Kondo and T. Hayashi, *Memoirs Coll. Agri. Kyoto Imp. Univ.*, No. 2, Art. 2 (1926).

according to the differences among the protein ionizing powers of the ions derived from the salt. Therefore, such a protein as casein or rice-glutelin under the presence of salts, cannot take an iso-electric form, even in the iso-electric solution. E. J. Cohn⁽¹⁾ has already stated that the presence of the foreign protein (with different solubility and different iso-electric point), of multivalent ions, or of neutral salts may shift the point of minimum solubility of the protein; hence the presence of these impurities renders impossible the determination of the true iso-electric point. This opinion may be reasonable from one point of view.

Moreover, if the concentration of the salt increase, the protein molecules may combine with one component of salt and form a complex compound. This complex-compound may be soluble or insoluble according to the concentration of the salt. Hence, the protein may not flocculate in a simple iso-electric form at the point of maximum flocculation in such a salt solution. These influences of salts on the iso-electric behavior of the protein are variable according to the kinds of salts and their concentration. The present work has for its purpose a more distinct elucidation of the above phenomena according to experimental results. The details are described in the Memoirs of the College of Agriculture, Kyoto Imperial University, No. 5.

Experimental Results and Conclusions. After the experiments described in the preceeding report⁽²⁾ we know that the rice-glutelin, studied in this work, can flocculate at the optimum at pH 5.38–5.08 in a 0.10 n. sodium acetate solution, which is 0.02–0.04 n. in respect to acetic acid. Therefore, we have now to study the influence of salts on the rice-glutelin in such an apparent iso-electric solution as described above. The experiments were undertaken with chlorides, for comparing the influences of the various cations. The results are shown in the following figures. The figures, marked with “a”, show the change of the iso-electric reaction, which forced after the addition of the various chlorides. And the figures, marked with “b”, show the change of the precipitability of the iso-electric rice-glutelin under the addition of the chlorides.

As shown in the next figures, untill the salt-concentration increases to a certain degree, the higher the concentration becomes, the less the precipitability of the rice-glutelin. This phenomena may be explained by our theory, that is, the higher the salt-concentration increases to a certain limit, the greater the difference in protein-ionizing power between the cations and anions derived from the salts. Hence, the protein molecule may ionize as much as correspondent with the difference of powers, and in

(1) E. J. Cohn, *Gen. Physiol.*, 4, No. 6 (1922), 697.

(2) K. Kondo, T. Hayashi and T. Matsushita, *Memoirs Coll. Agri. Kyoto Imp. Univ.*, No. 2, Art 3 (1926).

result the protein may dissolve a part. This is one of the principles on which the so-called solvent action of the salt on the protein is based. However, if the salt-concentration increase over the limit, the salt or one of its components may combine with protein and result in a further precipitation. This precipitation may be due to the formation of a complex compound

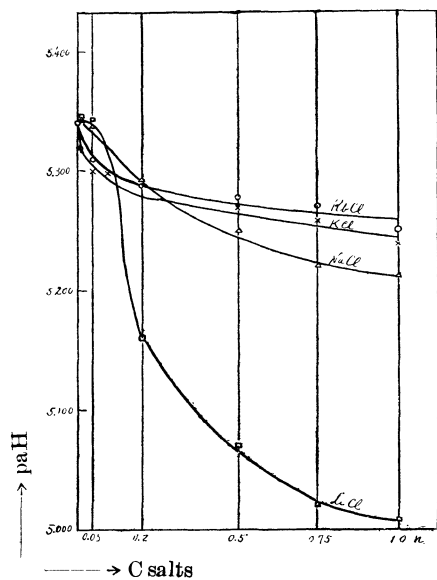


Fig. 1 a.

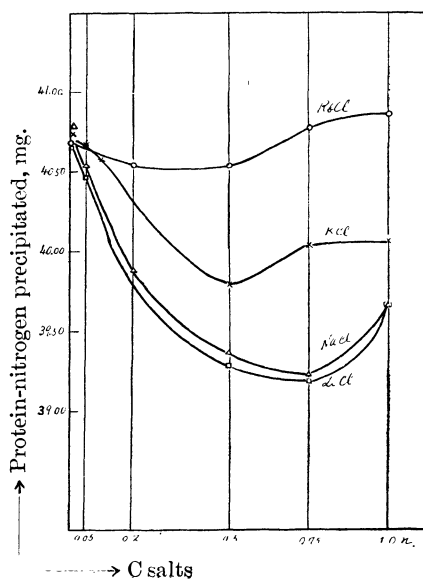


Fig. 1 b.

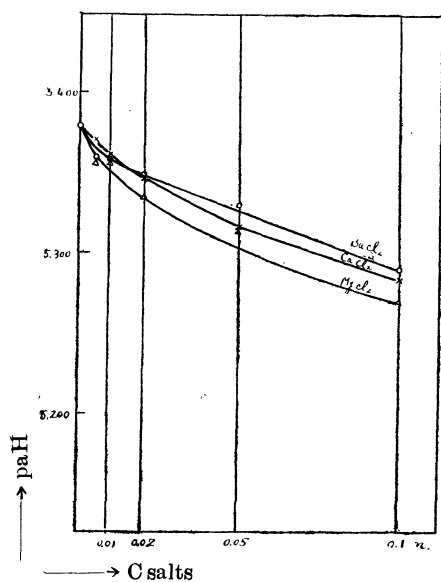


Fig. 2 a.

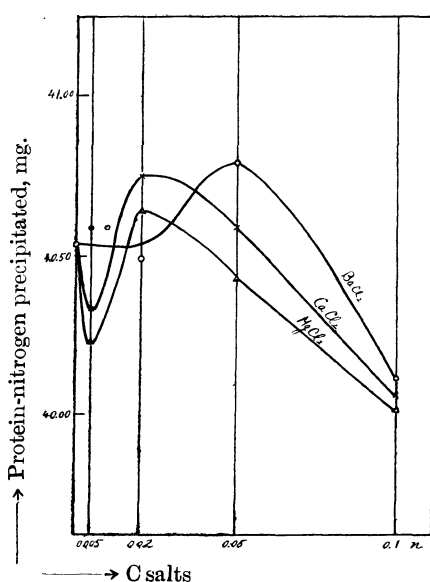


Fig. 2 b.

combining the protein and one component of the salt. This may be an original principle of the so-called precipitating action of the salt on the protein. Then, the protein-precipitate here obtained may consist of the mixture of the non-ionic rice-glutelin and the complex-salt-formed rice-glutelin. Therefore, we can not assume the reaction of the solution, in

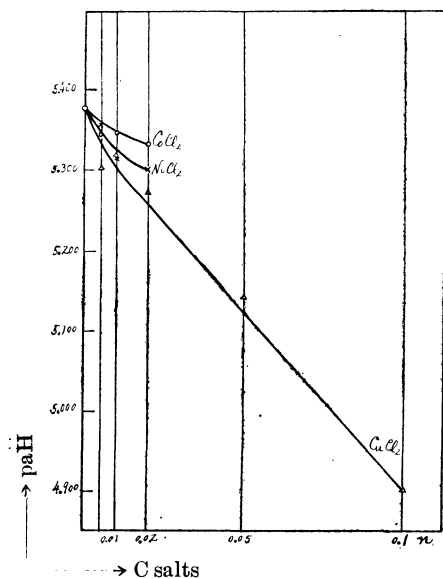


Fig. 3 a.

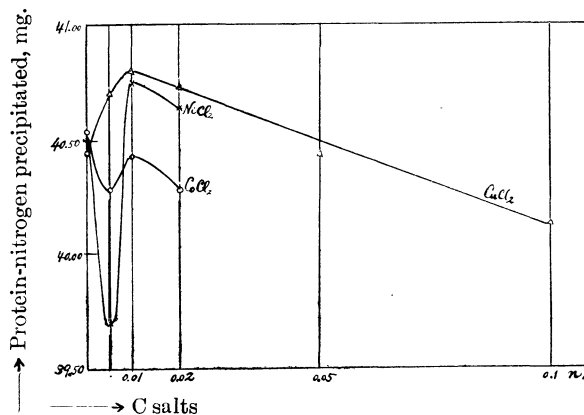


Fig. 3 b.

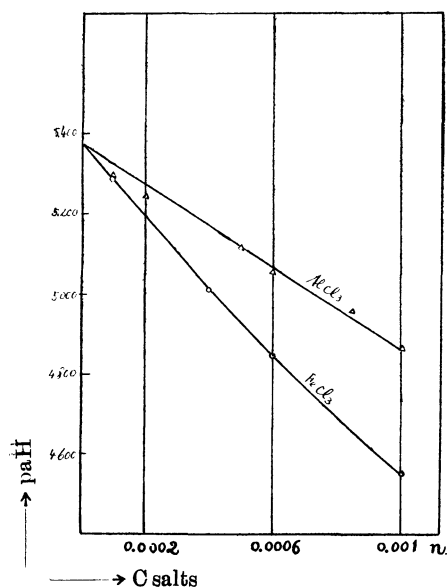


Fig. 4 a.

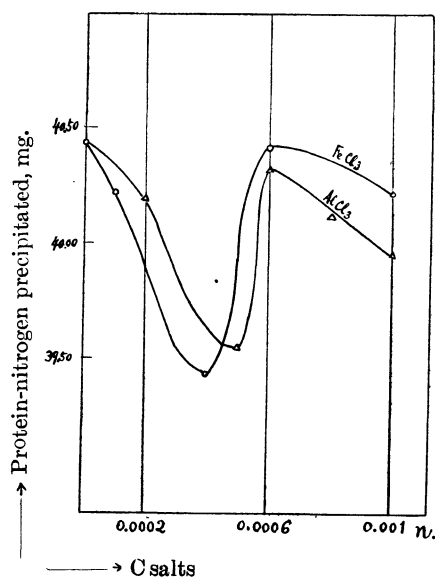


Fig. 4 b.

which, though the precipitability of the protein increased to a maximum point, to be an iso-electric reaction of the protein, when the salt-concentration is high. Because, the protein may not precipitate in all phases of the simple non-iogenic form in such a solution.

However, if the salt-concentration increase more than the above limit, the amount of the precipitated protein will decrease gradually in accordance with the salt-concentration. This may be due to the formation of a soluble or dissociable complex-compound formed of the protein and the cations derived from the salt. From other data⁽¹⁾ it may be inferred that a protein forms a complex-salt with one component of an inorganic salt. Moreover, the higher the concentration of the salt becomes, in a parallel manner, the greater the activity of the hydrogen ion, but the precipitability-curves turn at a certain salt-concentration. Herewith we are able to confirm the proposition that the salt itself, as well as the hydrogen ion activity, may play a great part in the rôle of the dissolution and precipitation of the protein. This action of the salt is due to the cations derived from the salt, and the action of the cations is peculiar to the kind of salt and its concentration. With chlorides we may arrange these cations with same valence in the order of their mobilities.

J. Loeb states that the influence of an acid, base or neutral salt on the physico-chemical properties of the protein solution is explained only by the valency rule. However, in the field, according to the phenomena alluded to, we must bear in mind the specific actions of ions as well as their valence. Therefore, we may agree with W. D. Bancroft, but not with J. Loeb, for the former sustains Hofmeister's rule which the latter does not.

Repeatedly going over the results shows us clearly that the influence of the chlorides on the behavior of rice-glutelin and the reaction of the solution becomes stronger with the increase of the valence of cations.⁽²⁾ In other words, the higher the valence of cations, the greater the difference, between chloride ion and cations in protein-ionizing power. That is, the precipitability curve of the protein has already been turned at the point of lower concentration of salt with the cations of higher valence. Therefore, in the presence of salt especially with multivalent ions, even in low concentrations, such a protein as rice-glutelin or casein may exhibit maximum flocculation at a hydrogen ion activity other than the iso-electric point of the protein.

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- (1) E. J. Cohn, *J. Biol. Chem.*, **59**, iv and vii (1925); J. H. Northrop and M. Kunitz, *J. Gen. Physiol.*, **7** (1924-25), 25; D. E. Greenberg and C. L. A. Schmidt, *J. Gen. Physiol.*, **8** (1926), 271.
 - (2) Hardy (*J. Physiol.*, **24** (1899), 288 & **33** (1905), 251), Mellanby (*J. Physiol.*, **33** (1905), 338), Osborne and Harris (*Am. J. Physiol.*, **14** (1905), 151) and Hopkins and Savory (*J. Physiol.*, **42** (1911), 189) have found that the solvent or precipitating action of salts upon globulins increases distinctly with the valence of their ions.

The same theory has been discussed by Cohn.⁽¹⁾ Hereupon, it is clear that the presence of the salt plays an important part in the determination of the iso-electric point of the protein.

According to the results in Figures 3 and 4, Cu^{++} , Fe^{+++} or Al^{+++} , even in low concentration, forms a complex compound with protein. We know that Cu^{++} is very poisonous for organisms, especially for algae and fungus. We know also that the presence of iron and alumina in the soil is considered as one of the sources in the formation of acid soil. The sterility of plants in such a soil may be due to inhibition of the life-process in the formation of a complex compound between Fe^{+++} or Al^{+++} in the soil and the protoplasm-protein of the plant cell as well as to the acidification of the soil-reaction. The mechanism of the poisoning action of Cu^{++} or other heavy metal ions on organisms may be explained by the conception described above.

Laboratory of Nutritional Chemistry,
The Institute of Chemical Research, Kyoto.

(1) E. J. Cohn, *J. Gen. Physiol.*, **4** (1922), 697.

STUDIES ON AMINO-ACID ANHYDRIDES, I.
MOLECULAR COMPOUNDS OF DIKETOPIPERAZINE WITH
COPPER HALIDES.

By Tei-ichi ASAHINA and Tsurumatsu DŌNO.

Received May 14, 1928. Published June 28, 1928.

Recently one of the authors and Prof. Y. Shibata have published two papers on the study of absorption spectra of several diketopiperazines.⁽²⁾ The motives of these works were to investigate the physical and chemical natures of these substances, the importance of which became to attract general attention in protein chemistry. In the present work, several behaviours of diketopiperazine on the formation of molecular compounds with some heavy metallic salts were studied. Such molecular compounds of amino-acids, polypeptides and amino-acid anhydrides with inorganic salts were first amply prepared by P. Pfeiffer and T. v. Modelski in 1912–1913.⁽³⁾ Pfeiffer and Fr. Wittka⁽⁴⁾ developed the studies and gave precise description of the molecular compounds of glycine anhydride with CaCl_2 , CaBr_2 , LiCl and LiBr ,

(2) Y. Shibata and T. Asahina, this journal, **1** (1926), 71; **2** (1927), 324.

(3) *Z. physiol. Chem.*, **81** (1912), 329; **85** (1913), 1.

(4) *Ber.*, **48** (1915), 1041 & 1289.

which had formerly been prepared by Pfeiffer and Modelski. Pfeiffer extended, with his co-laborators, those studies and showed various points of importance in producing the molecular compounds containing inorganic salts in the chemistry of protein and amino-acids.⁽¹⁾ As to the behaviours of diketopiperazine to organic matters, Powarnin and Tichomirow⁽²⁾ described that glycine anhydride gave molecular compounds with poly-phenols. From their experimental results they suggested an *addition theory*, in opposition to the *peptisation theory*, on the chemism of tanning. Pfeiffer, with Olga Angern and Liu Wang, prepared several addition compounds of glycine anhydride and sarkosin anhydride with phenol derivatives, aromatic amines and some amino-acids and its derivatives.⁽³⁾

They also prepared the molecular compounds with phenol and amine derivatives of various azo-compounds, most of which are in actual use in dyeing. As the results of their so-called "Modellversuche" they proposed, on the theory of dyeing, a view that dyestuff-adsorption on the surface of wool and silk fibres is nothing but the formation of molecular compounds caused by the saturation of residual affinities of the molecules of dyestuffs and albuminous substances.⁽⁴⁾ On the other hand the important rôle of salts of alkali-earth metals in the polymerisation of proteins, was elucidated by Prof. K. Shibata.⁽⁵⁾

The molecular compounds of diketopiperazines, mainly described up to the present time, by Pfeiffer may be classified in the following manner :

Mol. comp. with alkali and alkali-earth halides.

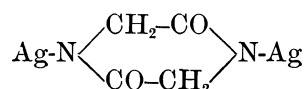
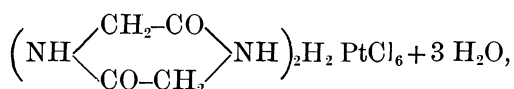
Mol. comp. with phenols, (prepared also by Powarnin and Tichomirow).

Mol. comp. with aromatic dyes (mainly azo-dyes).

Mol. comp. with amino-acids.

Mol. comp. of enolic diketopiperazines with each other.⁽⁶⁾

One more class, also, can perhaps be added to i.e. molecular compounds with heavy metallic salts. Of such a type of compounds, the authors could find, in chemical literature, only those described by Th. Curtius and F. Göbel.⁽⁷⁾



(1) P. Pfeiffer, "Organische Molekülverbindungen" (1927).

(2) Chem. Zentr., (1924), III, 857.

(3) Pfeiffer, O. Angern and L. Wang, Z. physiol. Chem., **143** (1925), 265.

(4) Pfeiffer and O. Angern, Z. angew. Chem., **39** (1926), 253; Pfeiffer and L. Wang, Z. angew. Chem., **40** (1927), 983.

(5) K. Shibata, Acta phytochimica, **2** (1924), 39 & 193.

(6) E. Abderhalden u. E. Schwab, Z. physiol. Chem., **164** (1927), 278.

(7) J. prakt. Chem., (2), **37** (1888), 178.

and [Glycine anhydride-copper],
but the latter two are salt-like compounds and not addition compounds.

Now, in this work, the present authors prepared the true molecular compounds of diketopiperazine with chloride and bromide of copper. Thus the readiness, with which glycine anhydride produces the molecular compounds with neutral heavy metallic salts, will be regarded due to the easy saturation of residual affinities, and the molecular compounds now obtained by the present authors, together with salt like compounds of Curtius and Göbel will probably be taken as "Modelle", as stated by Pfeiffer, for the compounds [protein- heavy metallic salts].

The molecular compounds of glycine anhydride with other heavy metallic salts have also been prepared by us; and the results will soon be reported in this journal.

Experimentals.

1. *Glycine anhydride-Copper chloride.*

Glycine anhydride (0.5 gr.) was dissolved in 20 c.c. hot water and to this, a warm solution of 5 gr. copper chloride (hydrate) in 5 c.c. water was added, the mixture was at once cooled under the tap; minute crystals of light blue colour soon separated out which, after standing overnight in a ice-chest, were drained, washed with a small quantity of ethyl alcohol (50%), and pressed between sheets of filter paper. Yield 0.9 gr. To the filtrate, equal volume of alcohol was added and after standing overnight in a ice-chest, 0.1 gr. of the same (but a little larger) crystals were obtained from this. Total yield 1 gr. (with regard to the glycine anhydride used, 80% of the calculation for $C_4H_6O_2N_2 \cdot CuCl_2 \cdot 2 H_2O$).

The compound has an aspect of a light blue rhombic needle; it is partly decomposed in water and alcohol. In the hot solvents the decomposition proceeds quicker and white crystals were obtained from the solution, which were identified, by microscopical examination (form, extinction, elongation) and also by the reaction proposed by Dr. Sasaki⁽¹⁾, to be the original glycine anhydride.

The glycine anhydride-copper chloride is insoluble and not or scarcely decomposed in acetone, benzene, ether and chloroform. On heating, the water of crystallisation is expelled at 110°C. and the compound turns reddish brown; on further heating it decomposes without melting.

It can only be recrystallised by dissolving in a warm concentrated solution of copper chloride and then cooling.

(1) *Biochem. Z.*, 114 (1921), 63.

Analysis

1. (a) Nitrogen

Sample	vol. of N ₂ (c.c.)	temp. (°C.)	press. (mm.)	% of N ₂
5.437 mg.	0.464	13.8	758.2	9.93
3.561 $\nearrow$	0.291	13.0	761.4	9.81
5.132 $\nearrow$	0.434	12.5	762.4	9.95
6.284 $\nearrow$	0.533	13.0	757.5	9.89
Calc. for C ₄ H ₆ N ₂ O ₂ •CuCl ₂ •2 H ₂ O,				9.84

(b) Nitrogen (dried at 120°C. in vacuum)

Sample	vol. of N ₂ (c.c.)	temp. (°C.)	press. (mm.)	% of N ₂
6.035 mg.	0.586	13.0	749.3	11.24
Calc. for C ₄ H ₆ N ₂ O ₂ •CuCl ₂ ,				11.20

2. Copper

Sample	CuO	% of Cu
2.765 mg.	0.769 mg.	22.22
0.3520 gr.	0.0977 gr.	22.10
0.2086 $\nearrow$	0.0573 $\nearrow$	21.95
0.4033 $\nearrow$	0.1132 $\nearrow$	22.44
Calc. for C ₄ H ₆ N ₂ O ₂ •CuCl ₂ •2 H ₂ O,		22.34

3. (a) Chlorine

Sample	AgCl	% of Cl ₂
4.117 mg.	4.104 mg.	24.67
6.440 $\nearrow$	6.395 $\nearrow$	24.57
6.445 $\nearrow$	6.413 $\nearrow$	24.62
0.1743 gr.	0.1722 gr.	24.50
Calc. for C ₄ H ₆ N ₂ O ₂ •CuCl ₂ •2 H ₂ O,		24.92

3. (b) Chlorine (dried at 120°C. in vac.)

Sample	AgCl	% of Cl ₂
3.810 mg.	4.270 mg.	27.73
6.748 $\nearrow$	7.510 $\nearrow$	27.97
Calc. for C ₄ H ₆ N ₂ O ₂ •CuCl ₂ ,		28.53

4. Water of crystallisation

Sample	weight loss (at 120°C. in vac.)	% of H ₂ O
15.523 mg.	1.915 mg.	12.57
10.415 $\nearrow$	1.305 $\nearrow$	12.53
20.156 $\nearrow$	2.553 $\nearrow$	12.67
Calc. for C ₄ H ₆ N ₂ O ₂ •CuCl ₂ •2 H ₂ O,		12.65

2. *Glycine anhydride-Copper bromide.*

Glycine anhydride (1 gr.) was well pulverised and brought into a brown solution of copper bromide. (4.5 gr. CuBr₂ in 20 c.c. water). The copper bromide solution had previously been prepared by dissolving freshly precipitated copper oxide from a known quantity of copper vitriol, in a little excess of hydrobromic acid (d=1.206) and concentrating in a vacuum desiccator over conc. sulphuric acid.

Soon after the addition of the glycine anhydride to this solution, bright green monoclinic crystals (tabular along b (010)) separated out. After 2 days the crystals were collected, drained and pressed between sheets of filter-paper. Yield 3 gr. (with regard to glycine anhydride used, 90% of the calculation for C₄H₆O₂N₂•CuBr₂•2 H₂O)

The compound can easily be decomposed by water, acetone and alcohol, giving white powders, which were identified to be glycine anhydride by the crystal form and Sasaki's reaction. It is insoluble in other organic solvents

the recrystallisation can be carried out by dissolving in copper bromide solution and then evaporating in the vacuum over conc. sulphuric acid.

Analysis

1. Nitrogen

Sample	vol. of N ₂ (c.c.)	temp. (°C.)	press. (mm.)	% of N ₂
15.070 mg.	0.971	15.5	765.5	7.53
Calc. for C ₄ H ₆ N ₂ O ₂ ·CuBr ₂ ·2H ₂ O,				7.50

2. Copper

Sample	CuO	% of Cu
0.2005 gr.	0.0424 gr.	16.89
0.2024 $\nearrow$	0.0433 $\nearrow$	17.09
Calc. for C ₄ H ₆ N ₂ O ₂ ·CuBr ₂ ·2 H ₂ O,		17.02

3. Bromine

Sample	AgBr	% of Br ₂
10.915 mg.	10.830 mg.	42.23
6.715 $\nearrow$	6.705 $\nearrow$	42.50
Calc. for C ₄ H ₆ N ₂ O ₂ ·CuBr ₂ ·2 H ₂ O,		42.79

4. Water of crystallisation

Sample	weight loss (dried at 100-105°C. in vacuum)	% of H ₂ O
0.5244 gr.	0.0511 gr.	9.74
Calc. for C ₄ H ₆ N ₂ O ₂ ·CuBr ₂ ·2 H ₂ O,		9.67

In order to determine whether these molecular compounds are formed in the solution to any extent, the spectroscopical method proposed by Prof. Y. Shibata with Dr. T. Inoue and Dr. Y. Nakatsuka,⁽¹⁾ was here applied. The maximum end-absorption was found, in both cases, when the molar proportion of copper salt to the glycine anhydride was (7-8): 1.

The degree of the compound formation seems to be quite small as the diagrams indicate, because the change of the wave lengths of the absorption end corresponding to the change of the molar proportion of the mixture was found to be rather small.

Fig. 1. Abscissa: The ratio of $\frac{\text{vol. (c.c.) of } \frac{1}{20} \text{ mol. aqueous CuCl}_2 \text{ soln.}}{\text{vol. (c.c.) of } \frac{1}{20} \text{ mol. aqueous C}_4\text{H}_6\text{N}_2\text{O}_2 \text{ soln.}}$

Fig. 2. Abscissa: The ratio of $\frac{\text{vol. (c.c.) of } \frac{1}{10} \text{ mol. aqueous CuBr}_2 \text{ soln.}}{\text{vol. (c.c.) of } \frac{1}{10} \text{ mol. aqueous C}_4\text{H}_6\text{N}_2\text{O}_2 \text{ soln.}}$

(1) *Japanese J. of Chem.*, **1** (1922), 1.

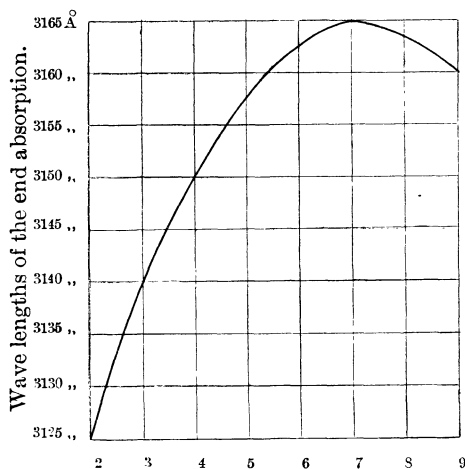


Fig. 1.

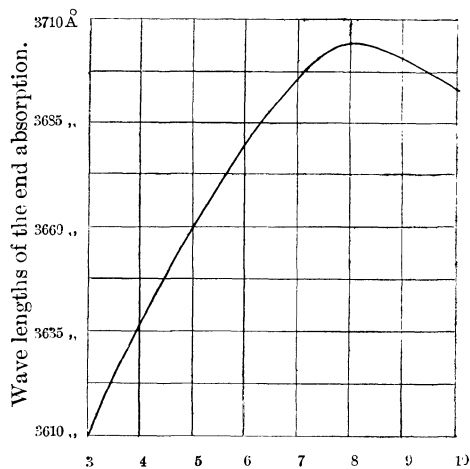
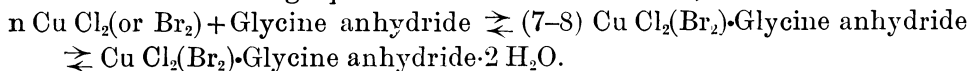


Fig. 2.

Thus the following equilibrium can be established,



The authors are continuing the work in using other metallic salts and amino-acid anhydrides.

The best thanks of the authors are due to Prof. Y. Shibata and Prof. K. Shibata for the kindness of encouragement and guidance extended from time to time. The cost of the research was partly defrayed from the grant of the Imperial Academy for which they also express their hearty gratefulness.

Summary

1. Molecular compounds of diketopiperazine with copper chloride and bromide were prepared.
2. The formation of such compounds in aqueous solution with formulae other than those obtained in solid state was ascertained.
3. The meaning of these molecular compounds for the chemistry of protein was discussed.

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DISPERSOIDOLOGICAL INVESTIGATIONS ON LATEX.⁽¹⁾By P. P. von WEIMARN.⁽²⁾

Received May 29, 1928. Published July 28, 1928.

In my investigations I used ammonia-preserved latex, *Hevea Brasiliensis*, (about 30% caoutchouc), *revertex*⁽³⁾ i.e. latex, concentrated to a paste-like condition (about 80% caoutchouc) and vulcanized latex i.e. *vultex*.⁽⁴⁾ In the programme of my investigations is also included the study of certain other kinds of latexes.

§1. **On the Structure of Latex.** The ultramicroscopic and microscopic investigations on preserved latex, I carried out by means of three apparatus: an immersion-ultramicroscope, after R. Zsigmondy; a dark-field condenser A (bizentrische Spiegelkondensor) with azimuth-stop; and a large bright-and-dark-field condenser; the two last from the firm of E. Leitz. In the work with these two apparatus was used a special oil-immersion objective 1/12-a (from the firm of E. Leitz; this objective has inside an intermediate fitting with an iris-diaphragm) and periplantic eyepieces $\times 12$ and $\times 25$ (i. e. the magnification was $1140\times$ and $2375\times$); the investigations were carried out not only at room temperature, but also at elevated temperatures, reaching to about 100°C .

T. Petch and W. Babilioff⁽⁵⁾ have stated that some of the particles in a fresh *Hevea* latex have a pear-like shape; certain particles have "tails"; Babilioff has also observed that latex from young parts of plants consists chiefly of round particles, whilst latex obtained from the trunk and roots contains a prevailing number of pear-like particles.

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- (1) In the present paper are summed up briefly the chief conclusions and results of the investigations carried out by me up to this time. The chief results were reported to the Imperial Industrial Research Institute of Osaka, on April 30, 1928. A detailed description with numerous photomicrographs and photo-ultramicrographs of separate latex particles as well as of various structures of latex coagula and jellies will appear in my papers in *Reports of the Imperial Industrial Research Institute of Osaka*.
 - (2) Translated from Russian by Mrs. P. P. von Weimarn.
 - (3) I wish to express here to The Dunlop Rubber Co. (Wakinohama, Kobe) my sincere thanks for kindly supplying latex and revertex for my investigations.
 - (4) The writer expresses his hearty thanks to Mr. W.C. Davey, of The Dunlop Rubber Co., for kindly preparing vultex for the present investigations.
 - (5) F. W. Hinrichsen und K. Memmler, "Der Kautschuk und seine Prüfung", (1910), Leipzig; B.D.W. Luff, "Die Chemie der Kautschuks", (1925), Berlin; Ernst A. Hauser, *The India Rubber Journal*, 68 (1924), 725; A. van Rossem, *ibid.*, 68 (1924), 1081 & 1123; H. Freundlich und E. A. Hauser, *Erganzungsband zur Koll. Z.*, 36 (1925), 15; Ernst A. Hauser, "Latex", (1927), Dresden; etc.

On the basis of his detailed investigations, Ernst A. Hauser⁽¹⁾ arrived at the conclusion that particles of sphere-like shape are very rare in Hevea latex, and the great majority of particles have oblong, egg-like, or pear-like shapes; certain of such particles have also "tails".

The investigations of V. Henri, T. Petch, Clayton Beadle and Henry P. Sterens, E. P. Wightman and A. P. H. Trivelli, Ph. Schidrowitz, W. Babilioff, Ernst A. Hauser, H. Freundlich and E. A. Hauser, and others⁽²⁾ have shown that the particles in ammonia-preserved as well as in fresh Hevea latex vary very greatly in size: in the latex obtained from the trunk of a tree of 10–15 years of age, the diameter of the particles varies between 0.5μ and 3μ ; besides such particles this same latex contains a great number of particles discernible only under the ultramicroscope. The dimensions indicated are those of the diameter of the cross-section of the particles, and not those of the length of particles. Their length reaches $4\text{--}5\mu$, and very seldom 6μ or more. The greater number of particles of latex from young plants and from green parts of old plants are ultramicroscopical, and the size of particles of the coarse-disperse part of these latexes scarcely ever exceeds 1μ .

The micro- and ultramicroscopical examinations, which I have carried out of ammonia-preserved latex, have shown that among microscopically visible particles are to be found particles of every shape which have been described by the above investigators. The ratio of the number of particles visible in the bright field of view (microscope) to that in the dark field (ultramicroscope) is less than 1, i. e. the number of ultramicroscopical particles is considerably greater than that of microscopical ones. This is most easily demonstrated when examining the latex diluted with water 300 times by means of a bright-and-dark-field condenser; on changing from the bright to the dark field, the increase in the number of visible particles appears striking.

From the *low* layers of a diluted latex (e. g. 1:300) poured into a *tall* cylinder and allowed to stand at room temperature more than 48 hours, it is possible, for investigation in the bright field, to prepare such a preparation in which not *one* single particle is revealed; however, by changing to a dark field, there are immediately observed numerous particles in a lively Brownian movement. A *really colloidal* latex may be obtained from diluted latex by the method of fractionating its particles on standing.

E. Hauser⁽³⁾ has established that the finest ultramicro-particles of Hevea latex have shapes different from spheres; i. e. one of their dimensions exceeds the others.

(1) l. c.

(2) l. c.

(3) E. A. Hauser, "Latex," 65.

My examination of latex by means of the immersion-ultramicroscope (the shape of diffraction rings) and by the dark field condenser A, from the firm of E. Leitz, with azimuth-stop and oil-immersion objective with aperture-stop, revealed that certain number of particles of ammonia-preserved latex possess the shape of either a sphere, or an ellipsoid not far removed from a sphere. Pear-like shapes, and shapes with tails, are not specific shapes for Hevea latex particles, but the same shapes are readily formed in emulsions of oils in water in the presence of emulsifiers, which cover the drops with a film; the consistency of this film must be considered as plastic-solid.⁽¹⁾

I have observed under the microscope particles of *every* shape appropriate to the particles of Hevea latex, i. e. oblong, pear-like, and with tails, in a preparation which I obtained by mixing one drop of immersion oil with one drop of concentrated aqueous solution of sodium iodide, or lithium iodide;⁽²⁾ the particles in this preparation are so large that for their investigation a magnification of only 500 fold is quite sufficient.

The investigations of E. Hauser and H. Freundlich⁽³⁾ of latex by means of the micro-manipulator, after Petérfi, has led them to the conclusion that the particles of latex are drops of a viscous liquid (the degree of viscosity may be compared with that of honey) surrounded with a film almost solid, and elastic. In their opinion, this film in its properties is near to raw caoutchouc.⁽⁴⁾ According to these investigators,⁽⁵⁾ the film, in its turn, is surrounded with an adsorption layer of proteins and resins. H. Freundlich and E. Hauser hold that latex from *Ficus elastica* consists of particles *perfectly* liquid and possessing no film of more solid („härtere“) consistency; the adsorption layer consisting probably of resins.

Thus, according to H. Freundlich and E.A. Hauser, a particle of Hevea latex is made up of caoutchouc in two conditions: solid without, and liquid within; the particle of *Ficus* latex consisting of caoutchouc which is in a liquid condition only. These two investigators advance the following explanation as probable for the two-phase condition of latex: (1) The homogeneous liquid phase of caoutchouc hydrocarbon is surrounded with a solid film of its polymer; (2) The liquid phase is not homogeneous, but represents a colloidal solution of a solid polymer in the liquid caoutchouc-hydrocarbon; the film is the gel of this colloidal solution. Consequently, in the

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- (1) Robert E. Wilson and E.D. Ries, "Colloid Symposium Monograph, I," (1923), 145. In fig. 18, the drop to the left of the picture, possesses one of the forms of the particles of Hevea latex.
 - (2) The photomicrographs of the drops of these emulsions will appear in one of my papers in *Reports of the Imperial Industrial Research Institute of Osaka*.
 - (3) E. A. Hauser, "Latex," 66-71.
 - (4) E. A. Hauser, "Latex," 70.
 - (5) H. Freundlich and E.A. Hauser, l.c. 24-25.

case of *Ficus elastica*, either no solid polymer is formed, or no coagulation proceeds on the surfaces of separation of drops of the iso-colloid solution (the term offered by Wo. Ostwald) of caoutchouc and of the dispersion medium (serum).

Formerly⁽¹⁾ I studied the processes of spontaneous disintegration into *gelatinous* spherulites of strongly swollen cellulose fibres, and also the processes of coagulation into gelatinous spherulites, of colloidal solutions of different substances. The *general* consistency of certain of these spherulites must be acknowledged as liquid, though the spherulites e. g. in the case of cellulose, are built up of minute pieces of *solid fibre* and of parts of fibrils, which are soaked with the viscous aqueous salt solution (e. g. of CaCl_2).

Under ultramicroscopic examination, the gelatinous cellulose spherulites reveal a structure (though often not quite distinct), because of the considerable difference in the optical properties of the disperse part and those of the dispersion medium in the gelatinous precipitates of cellulose. In those cases when the optical properties of the liquid soaked up by the gelatinous spherulites approach the optical properties of the solid substance of these spherulites, they of course appear optically homogeneous under the ultramicroscope, and no structure whatever can be revealed in these gelatinous spherulites. Such a proximity of optical properties exists in the case of iso-colloidal solutions of caoutchouc.

The comparison of certain photomicrographs taken of Hevea latex by H. Freundlich and E. Hauser⁽²⁾ and especially of the photomicrograph taken by H. Green of the latex from *Ficus elastica*,⁽³⁾ with the photomicrographs and photo-ultramicrographs which I have taken of the cellulose gelatinous spherulites, has led me to the idea that in the cases of certain latexes of caoutchouc we are dealing with *emulsion-suspensions of gelatinous iso-spherulites*. It is more than probable that these spherulites belong to the forms of the aggregate-fluid-crystalline state.⁽⁴⁾ Especially the picture represented in the photomicrograph taken by H. Green shows a striking resemblance to the pictures of cellulose spherulites in the photomicrographs taken by me.

The temperature must be taken into account as a factor acting upon the consistency of these iso-spherulites. My investigations have shown that *certain* of the latex particles flow together into larger particles; when the

- (1) P. P. von Weimarn, Dispersoidological Investigations XXII, Part II, Chapter II. § 2, Plates X-XI, *Reports of the Imperial Industrial Research Institute of Osaka*, (June, 1928).
- (2) H. Freundlich und E. A. Hauser, *Erganzungsband zur Koll. Z.*, 36 (1925), Tafel II, figs. 10 und 10 a.
- (3) E. A. Hauser, "Latex," 130, Fig. 55.
- (4) P. P. von Weimarn, *Reports of the Imperial Industrial Research Institute of Osaka*, Vol. VIII, No. 13 pp. 41-66. (November, 1927); *Koll. Z.*, 44 (1928), 279.

temperature is raised (to about 100°C.) the instances of such a union of particles become more numerous.

As I have had no micro-manipulator at hand, I have studied the consistency of particles, of their interior as well as of the external skin, by crushing between the cover- and object-glasses the largest particles found in the preparation of latex; the crushing was produced by a more or less strong pressure upon the preparations. In order to deform the particles of latex, I moved in one direction or the other the layer of latex, strongly pressed between the cover- and object-glasses. Under such manipulations, some of the pear-like particles of latex burst, and their liquid contents assumed the forms suggestive of a gelatinous consistency. By deforming the micro-particles of latex, I imparted to them various shapes, even shapes with concave surfaces and sharp angles; these shapes persisted in the particles during all the time of my observations.

By these and similar facts it is unequivocally shown that the film around a particle of latex cannot be likened to the film of raw caoutchouc, which, as is known, possesses considerable elasticity. The consistency of the films around the particles of latex is plastic solid to the same extent as is a film of fibroin-jelly (natural silk), or a film appearing on the surface of separation in the system: immersion oil + aqueous NaI or LiI solution.

I do not admit as sufficient the arguments of H. Freundlich and E. Hauser to the effect that the film by which the "liquid" contents of the particles of Hevea latex is surrounded, is a *pure* gel (or a *pure* polymer) of caoutchouc. In my opinion, the film is of a mixed composition, and is formed of complex particles: of subultramicro-particles of caoutchouc which are intermixed with particles of protein (as also with particles of resins and of other substances from serum).

I shall return to this subject later; now I wish to formulate my chief conclusion on the structure of Hevea latex, arrived at, after the study of the works of earlier investigators, on the ground of my micro- and ultramicroscopical investigations: *Latex is a poly-disperse system of iso-aggregate particles (iso-spherulites), the general consistency of which is fluid-gelatinous. The individual solid particles which compose the iso-aggregate particles of latex are very small, and the greater part of them is invisible under the ultramicroscope; the constituent parts of serum (i. e. the dispersion medium in which the iso-aggregate particles are suspended), viz. proteins, water, resins etc. in various concentrations, are present not only in the surface film, but also inside of the iso-aggregates; these non-caoutchouc components play corresponding rôles in the changes the iso-aggregates undergo in their consistency and structure, during the drying up and during other coagulation processes of latex.*

In accordance with the view previously expressed by me on the caout-

chouc-like state of matter, the high elasticity appropriate to this state is due to the presence in the viscous-liquid, or liquid-gelatinous medium, of a definite quantity of solid structure elements,⁽¹⁾ which possess the ability of becoming spirally curled (after the release from tension).

§2. The Gelatination of Latex and Revertex by Means of Extremely Concentrated Aqueous Solutions of Substances Appearing as Dispergators for Proteins. As is known, C. O. Weber⁽²⁾ drew a sharp difference between the coagulation of caoutchouc from latex containing proteins, and the coagulation of caoutchouc freed from proteins. The latter case of coagulation C. O. Weber called *coalescence*. The caoutchouc obtained by means of coalescence, Weber considered inferior to that obtained by means of coagulation. Later on, this opinion of Weber has been refuted by other investigators (see W. Esch, l. c.) and Weber himself finally wrote that the caoutchouc obtained by precipitation, by means of an ether solution of hydrochloric and formic acids from the solution in ether of caoutchouc freed from proteins, is of very high quality („einen sehr *hochklassigen* Kautschuk darstellt“).

According to my view, the gelatinous iso-spherulites of Hevea latex suspended in the serum, are surrounded by a *plastic-solid* transition layer, or by a film of a mixed composition, chiefly consisting of protein and caoutchouc, and therefore, the decrease in the amount of protein in this layer produces its more gelatinous consistency. Such a consistency of the particles of latex causes their sticking together, which produces a network tissue; under conditions of experimenting rightly selected, this tissue imbibes the whole of the mother solution, i. e. there ensues a *complete gelatination* of latex.

I undertook the study of the precipitation of Hevea latex by extremely concentrated solutions of LiI, LiCNS, Ca(CNS)₂, NaI, Ca(NO₃)₂, CaCl₂ etc., of poly-phenols, e. g. pyrogallol and resorcinol, thiourea and guanidine thiocyanate, because I had formerly proved⁽³⁾ the dispergative action upon proteins (e. g. fibroin-silk) of concentrated aqueous solutions of extremely soluble substances inclined to hydration. The experiments were carried out at room temperatures, and also at elevated temperatures (up to 170°C.).

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- (1) P. P. von Weimarn, Dispersoidological Investigations, XXI, *Reports of the Imperial Industrial Research Institute of Osaka*, (November, 1927). I have also studied the micro- and ultramicro-structure of caoutchouc coagula and jellies obtained from latex and revertex; the results of this study will appear in the *Reports of the Imperial Industrial Research Institute of Osaka*, with photomicro- and photo-ultramicrographs appended. Under very different conditions of coagulation of Hevea latex, fibrous coagula are easily obtained; the fibres possess spirally curled fibril structures.
 - (2) See e. g. W. Esch, *Chemiker-Zeitung*, 29 (1905), 267.
 - (3) P. P. von Weimarn, Dispersoidological Investigations, XI, *Reports of the Imperial Industrial Research Institute of Osaka* (March, 1926); Dispersoidological Investigations, XVII, *ibid.*, (June, 1927).

I have also carried out experiments on the coagulation of latex by means of extremely concentrated aqueous solutions of acetic acid and potassium hydroxide, because the proteins (e. g. fibroin) become dispergated also by the action of concentrated solutions of acids and alkalies, though in this case, the mechanism of dispergation is different from that in the case of salts, and is accompanied by a more or less deep disintegration of the molecules of proteins.

Besides this, I studied the influence upon Hevea latex of concentrated aqueous solutions of substances, which, with the concentration obtainable under ordinary pressure, prove to be aggregators for proteins (sodium citrate, potassium-sodium tartrate, and potassium sulphate). The following is observed when to a definite volume of latex (or to properly diluted revertex) is added a definite volume (e. g. equal) of a concentrated solution of one of the above-stated substances.

A. The temperatures and the concentrations of the solutions of substances-dispergators for proteins are such that the dispergation of proteins, which are in the latex, cannot proceed at all rapidly. Under these conditions, the latex, at least for several days, does not coagulate, or it yields an incoherent gruel, which is easily shaken down into a system of liquid consistency.

B. The temperatures and the concentrations of the solutions are such as to produce a rather rapid dispergation of proteins. Under these conditions, the formation of *one* piece of a coherent jelly is observed immediately or after the lapse of a short time. This phenomenon is produced by solutions of LiCNS, LiI, $\text{Ca}(\text{CNS})_2$, of concentrations attainable at room temperature. LiI and LiCNS are most powerful dispergators for proteins. When, at room temperature, latex is poured into a test-tube containing an equal volume of LiI or LiCNS-solution (approximately saturated at room temperature) and this mixture is shaken several times, there is immediately observed a complete gelatination; owing to syneresis, subsequent to the gelatination, the rod of elastic jelly can be easily taken out of the test-tube. The process of the complete gelatination of caoutchouc may be demonstrated very successfully as follows: into a test-tube of about 2 cm. diameter, containing 10 c. c. of an aqueous LiI-solution, *saturated* at room temperature, are poured 10 c. c. of ammonia-preserved latex, very carefully, along the walls of the test-tube (in order to prevent mixing). After closing the mouth of the test-tube with the finger, the contents are strongly shaken (only *once* is enough, after some practice); the shaking producing immediate gelatination. After the lapse of several minutes, if the finger is slowly withdrawn from the mouth of the test-tube, the whole rod of jelly follows, hanging on the film which has stuck to the finger.

The elastic properties of this rod possess a distinct vectoriality; the stretching force being constant, the rod of jelly may be elastically drawn out to a considerably greater extent in the direction of its length (i. e. in the direction in which the shaking has been performed; —here must be kept in mind the “aggregation by stretching”) than in the direction perpendicular to its length; the breaking strain of the rod is also greater when stretching in the direction of its length. This vectoriality is in full accord with my view on the caoutchouc-like state of matter (§ 1).

By such a gelatination may be obtained coherent pieces of caoutchouc of any desired form: it is possible to mould plates, or objects of complicated shape.

By mixing latex or revertex with the solution of a substance-dispersator for proteins, with the concentration suitably selected (the experiments being carried out at a suitable temperature), I prepared a thick uniform liquid or gruel; after pouring it into a mould, I placed the latter into a closet, keeping a suitable temperature; after a certain time, the contents of the mould became one single piece of a coherent jelly; owing to its contraction, (syn-eresis) the jelly could be easily taken out of the mould for the purposes of washing and further treatment. The objects thus moulded can be subjected to cold vulcanization.

C. The higher the temperature at which proceeds the coagulation of latex by the substances which disperse protein, the stronger (tensile strength) is the coagulum obtained; the coagula possess high degrees of elasticity. In suitably arranged experiments on coagulation at progressively increasing temperatures, the series of coagula obtained, possess definite mechanical properties, namely, under equal loads, the least elongation is found in the coagulum obtained at the highest temperature.

D. The solutions of substances appearing as substances-aggregators for proteins (e. g. sodium citrate, potassium-sodium tartrate, potassium sulphate) do not cause the coagulation of caoutchouc, for several days at least; or when they cause the coagulation, it proceeds by way of flakes or gruel, easily shaken up into liquid. For instance, after mixing latex with an equal volume of a concentrated aqueous sodium citrate solution (462 gr. of salt in 1 litre of the solution) the resulting system remained mobile (liquid) after the lapse of one month; a thick cream was formed near the surface, which by shaking dispersed into a mobile liquid.

When latex is being poured into *boiling* concentrated solutions of salts-aggregators for proteins (potassium sulphate, sodium citrate, potassium-sodium tartrate), and the boiling is continued for some time, the latex at first coagulates into tiny flakes, but on further boiling these flakes become agglomerated into *one* large, *loose* flake. This flake can be easily torn, it does

not possess the great tensile strength of the coherent coagula of caoutchouc obtained by pouring latex into *boiling* concentrated solutions of substances-dispergators for proteins.

It should be pointed out that there is no correspondence between facts and the widely accepted view, that only from latex (or generally from disperse systems of caoutchouc) *freed* from proteins, coagulation produces a coagulum in *one* piece.⁽¹⁾

Although the solutions of substances-dispergators (but not the *destroyers* of proteins) and also the solutions of substances-aggregators of proteins, do not of course free the latex from the proteins, they produce (the substances-aggregators at a slower rate) at *elevated* temperatures, at the end of the coagulation, *one* single piece of coagulum. At *room* temperatures, only the solutions of substances-dispergators of proteins (see above) effect the gelatination of latex into one coherent, elastic body.

By mixing at room temperature, for instance in a test-tube, Hevea latex with an equal volume of concentrated (96–99%) acetic acid, after shaking there is observed the formation of a rod of jelly which rapidly synerizes; the serum yielded is non-translucent, or only scarcely, when observed through a test-tube of 2 cm. diameter; it is of a greyish colour, and displays under the ultramicroscope a great number of particles in a lively Brownian movement; the aggregates of particles are also present. This turbid serum has not cleared up after the lapse of one month. A slightly turbid, though perfectly translucent, serum is obtained even after the shaking of only several drops of latex with 25 c.c. of 96% acetic acid.

When exactly similar experiments are carried out with extremely concentrated solutions of KOH, the process of the rod formation in the jelly is slow; the process goes only by creaming; on shaking in a test-tube latex with an equal volume of extremely concentrated KOH, there is formed at first a mobile gruel, which gradually becomes thickened, contracted and lifted to the surface (creaming), releasing at the bottom a transparent yellow serum. Already after the lapse of fifteen minutes, nothing flows out on turning the test-tube upside down, because the serum is closed by the thick gruel formed at the top of the test-tube. After the lapse of 24 hours, one third of the system from the bottom represents a transparent yellow serum; the remaining two-thirds being a rod of soft jelly; the jelly can be taken out as a whole by breaking the test-tube. After the washing of such a rod of jelly with water, the latter becomes turbid; if the rod be pressed under the water, the water becomes quite turbid and opaque. This fact shows that the particles of latex have not all as yet solidly grown together.

(1) Compare the experiments of E. A. Hauser ("Latex", 97) on the coagulation of latex, in which the protein was digested („verdauen“) by the addition of trypsin.

Thus, the solutions of those substances, which disperse protein, at the same time destroying it (extremely concentrated acids and alkalis) cause certain secondary phenomena.

By juxtaposition of the results communicated, the following conclusion is arrived at: *By mixing under suitable conditions latex with the solutions of any substance by which the proteins are dispersed, but the caoutchouc is neither dispersed nor destroyed, a complete gelatination of latex into one coherent, elastic body may be attained.*

It is of interest to dwell a little on the solutions of proteins⁽¹⁾ in the solutions of salts-dispersers for proteins;⁽²⁾ I shall confine myself to only one example: into a boiling (at 170°C.) aqueous solution of a mixture of LiCNS and LiI, was poured Hevea latex, and by means of boiling, the temperature was again raised to 170°C. The caoutchouc deposited in *one* elastic piece, which possessed an extremely high tensile strength; to the naked eye, the piece appeared as of a thread-like structure; it gave the impression of being composed of thin threads tangled and stuck together (they are thin streamlets of the ropy stage in the process of precipitation of caoutchouc).

After taking out the lump of caoutchouc, the remaining hot, transparent solution was diluted with a great amount of alcohol; an opalescence developed at once, then fine flakes appeared in the whole mass of the liquid. After the lapse of 15 minutes, the greater part of these flakes collected into several larger flakes, which gradually deposited on the bottom; the flakes are voluminous and appear yellowish in transmitted light. On diluting the same solutions with great amounts of water, instead of alcohol, a slight turbidity also appears, which gives rise to fine flakes, precipitating with great difficulty; in this case, the number of flakes (the quantity of precipitate) is considerably less than in the case of dilution with alcohol.

§3. On Complex Coagula of Caoutchouc with Proteins and Polysaccharides. I have obtained coagula of a mixed composition: Caoutchouc + silk (fibroin); caoutchouc + casein; caoutchouc + cellulose; caoutchouc + chitin and caoutchouc + keratin. These complex coagula are very easily obtained by the coagulation of latex produced by pouring (or pulverizing) into it the solutions of silk, casein, cellulose, chitin and keratin in concentrated aqueous solutions of substances (see above) which are dispersers

(1) On the protein of caoutchouc, see the interesting works of D. Spence, *The India Rubber Journ.*, **34**, 766; **35**, 23. Abstracts: *Koll. Z.*, **3** (1908), 103 etc.

(2) On pouring latex into a boiling, extremely concentrated, aqueous solution of pyrogallol, the coagulation of latex proceeds into one lump, as has been stated above. When this lump is taken out of the fairly translucent mother solution, and the latter is lavishly diluted with water, a milky-white, non translucent disperse system is formed. In this case as well as in certain others, the nature of the disperse phase of this turbid liquid is as yet not ascertained; the investigation is being continued.

for proteins and poly-saccharides. In the case of using fibroin, casein and keratin, the complex coagula obtained must be in addition treated with the solutions of substances which appear as substances-aggregators for proteins (i. e. for fibroin, casein and keratin).

As soon as I have investigated the mechanical properties of these coagula, I shall communicate in detail the results of my experiments in the *Reports of the Imperial Industrial Research Institute of Osaka*.

§4. On the Gelatination of Vultex. Since after vulcanization the particles of latex become less plastic and less liable to mutual union than before vulcanization (I refer to the union of the caoutchouc contents of the particles), it may be a priori expected that a wet rod of jelly obtained from *vultex* (by shaking in a test-tube an equal volume of vultex carefully poured into an aqueous solutions e.g. a LiI-solution, saturated at room temperature) will possess tensile strength *considerably* less than does a rod of jelly obtained by the same method from latex.⁽¹⁾ And on the ground of the fact that after vulcanization the particles of latex do not lose their capability to unite under a more or less strong compression, it may be also predicted that the above jelly of vultex, after its compression will acquire elasticity and greater tensile strength. The experiments carried out in this connection have fully confirmed all my above expectations: the wet rod of vultex jelly obtained can be easily torn to pieces and after compression, e. g. even under a cork-press, acquires mechanical properties of a higher order than before.

Good elastic films not only of latex, *but also of vultex*, are obtained by pouring latex and vultex onto large watch glasses and allowing the water to evaporate freely. Without pressure, the caoutchouc contents of the particles of vultex do not rapidly unite and do not form an elastic resistant body; in the case of film formation, the compression is fulfilled by kapillar, surface forces: the adsorption layers of the particles of vultex, consisting of proteins and resins, flow together when the particles come in contact. With progress of the evaporation of water, these non-caoutchouc layers, which have flown together, become contracted and exert considerable pressure upon the caoutchouc contents of the particles, forcing these contents to unite and to form a strong, resistant, elastic body. In no way am I in agreement with the view⁽²⁾ that *elastic* films of vultex result from the gluing together of the non-caoutchouc layers of vultex particles; I assert that the *elastic* films of vultex are caused by the gluing together (union) of the *caoutchouc contents* of particles.

(1) On the basis of my micro- and ultramicroscopic investigations, I arrived at the conclusion that in other aspects, i.e. in the form of the particles and in the structures of the coagula, no essential difference exists between latex and vultex.

(2) Ernst A. Hauser "Latex," 130-131.

By the results of my ultramicroscopic investigations of the structure of jellies and films of latex and vultex is established with certainty that their *inner* structure is fibril ; the thickness of separate fibrils is less than that of latex or vultex particles, and in no case does their minimum thickness exceed the dimensions of several molecules (because there is *fibril⁽¹⁾ cleavage*); they may possess even monomolecular thickness.

In conclusion I have to thank Mr. I. Shoji, D. Eng., President of the Imperial Industrial Research Institute of Osaka, for the opportunity of carrying out these investigations and for the permission to publish the results in this journal.

April-June, 1928.

The Dispersoidological Department of
the Imperial Industrial Research Institute of Osaka.

A MICROANALYTICAL DETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS BY TITRATION.

By **Bennosuke KUBOTA** and **Sadahiko HANAI**.

Received June 9, 1928. Published July 28, 1928.

Introduction. The determination of sulphur in a few milligrams of organic material may be carried out by the methods of F. Pregl.⁽²⁾ Though the methods are quite excellent, they involve some inconveniences in the performance of experiments. For instance, the special apparatus "Micro-Neubauer crucible" must be used for carrying out the gravimetric determination and the material to be analysed must contain neither nitrogen nor halogen for the volumetric one.

One of the authors⁽³⁾ had observed that the most active part of reduced nickel decomposes organic sulphur compounds (for instance thiophen) quantitatively in the hydrogen atmosphere and, while changing itself into nickel sulphide, it absorbs the sulphur completely.

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- (1) P. P. von Weimarn, *Reports of the Imperial Industrial Research Institute of Osaka*, Vol. VIII, No. 6, 22-29, (June, 1927).
 - (2) F. Pregl "Die quantitative organische Mikroanalyse", 2 ed. (1923), 122.
 - (3) B. Kubota & K. Yoshikawa, *Japanese Journal of Chemistry*, 2 (1925), 45; *Scientific Papers of the Institute of Physical and Chemical Research*, No. 39 (1925), 223.

It seemed to us that this process might be carried out with all sorts of organic sulphur compounds and that it might make possible of microanalytical determination of sulphur in organic compounds by titration without any inconveniences above mentioned. Thus the studies of this process with several kinds of organic sulphur compounds were undertaken and the confirmation of the correctness of this view was obtained by the results, shown in the table on page 172, which gave complete satisfaction.

Experimental. In order to analyse by this method, a few milligrams of the material is weighed in an open small platinum boat just as for the Pregl's micro-determinations of carbon and hydrogen. It is then introduced into a small decomposition tube of an outer diameter of about 10 millimeters and of a length of about 400 millimeters which rests on F. Pregl's combustion stand, and is placed behind the reduced nickel previously prepared in this tube by the action of pure hydrogen at about 250°C. on 10–15 gr. of nickel oxide which was obtained by the calcination of pure nickel oxalate free from sulphur and allowed to cool in the current of hydrogen. Closing the one end of the decomposition tube with the rubber stopper provided with a tapered glass tube through which a current of purified hydrogen gas passes and drives the air out of the decomposition tube, the outlet of which is immersed into a water basin as shown in Fig. 1. The hydrogen is made from zinc and hydrochloric acid and passed through the tubes of sodium hydroxide solution, concentrated sulphuric acid, heated metallic copper and sodium hydroxide successively. The front portion of the decomposition tube is carefully heated with a tube burner and the temperature is raised to about 200°C. After the tube has been freed from air, the small roll of wire gauze and the burner being moved towards the boat, the material is rendered to volatilize and allowed to pass very slowly over the catalyst by means of cautiously regulated hydrogen current. When the whole of the material to be analysed has finally passed over the catalyst, the heating of the decomposition tube is ceased and the contents of the tube are left to cool.

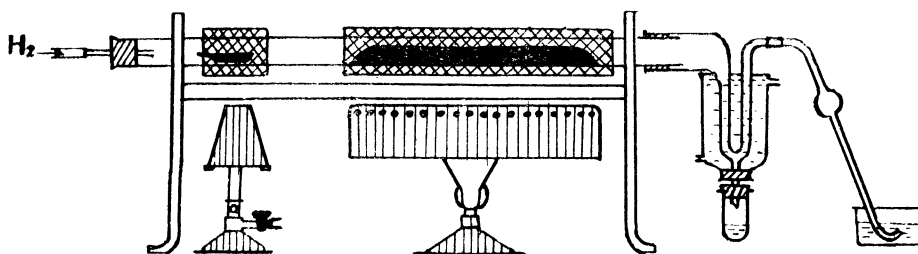


Fig. 1.

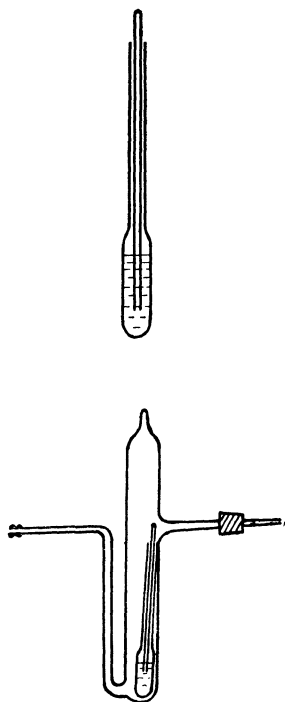


Fig. 2.

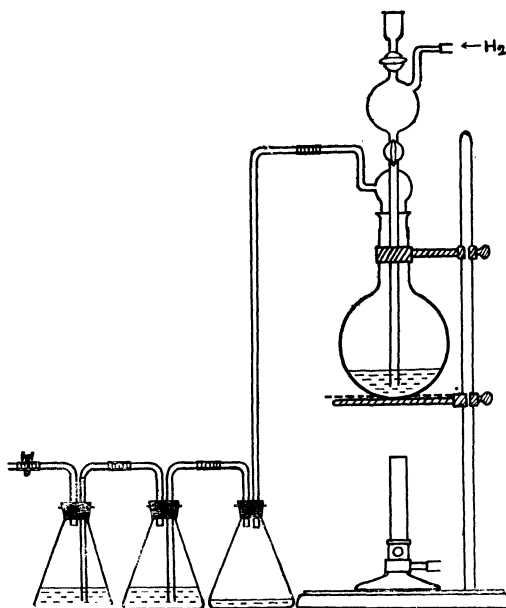


Fig. 3.

They are now subjected to the determination of sulphur by means of ordinary method of determination of sulphur in metallic sulphides: when the whole contents of the decomposition tube is dissolved, in a flask shown in Fig. 3, into a concentrated hydrochloric acid solution in the hydrogen atmosphere, the hydrogen sulphide gas is evolved at the same time that the hydrogen is produced. Being swept out by the current of pure hydrogen delivered from reservoir, this gas mixture passes through an ammoniacal cadmium solution (20 gr. $\text{CdCl}_2 + 400 \text{ c.c. H}_2\text{O} + 600 \text{ c.c. ammonia water}$, sp. gr. 0.96) and produces the precipitation of cadmium sulphide. This is filtered off and the residue is oxidised by an excess of an iodine solution which is obtained by the action of the potassium permanganate solution (approximately 0.08 N.) on the solution of potassium iodide (30 gr. $\text{KI} + 10 \text{ gr. NaHCO}_3 + 1000 \text{ c.c. H}_2\text{O}$). The amount of potassium permanganate used is estimated by the titration with sodium oxalate solution. The volumetric analysis of iodine employed in the oxidation of cadmium sulphide is then carried out by means of a 0.02 N. solution of sodium thiosulphate in the presence of starch solution. The percentage of sulphur in the material can then be calculated as follows,

$$\frac{\text{S}}{\text{Na}_2\text{C}_2\text{O}_4} \times a \times \frac{T_1 - T_2}{T_1} \times \frac{100}{P} = 23.93 \times a \times \frac{T_1 - T_2}{T_1 P} = \% \text{ of S.}$$

where P represents the weight of the material to be analysed, a the weight of $\text{Na}_2\text{C}_2\text{O}_4$ just oxidised by 10 c. c. of potassium permanganate solution, T_1 the volume (c.c.) of the $\text{Na}_2\text{S}_2\text{O}_3$ solution used for the oxidation of the iodine produce by the action of 10 c.c. of the KMnO_4 solution on KI , T_2 the volume (c.c.) of the $\text{Na}_2\text{S}_2\text{O}_3$ solution used for the oxidation of the iodine which is produced by the action of 10 c.c. of KMnO_4 solution on KI and is remained unchanged, not being used for the oxidation of the cadmium sulphide.

In the case of materials which volatilize with difficulty and by being heated in the hydrogen atmosphere decompose and leave some residue in the boat (for example ammonium bromocamphor-sulphonate and barium benzene-sulphonate in the table on page 172), it is necessary, after weighing the material in the boat, to cover it with reduced nickel which is prepared at the same time with the catalyst from pure nickel oxide in a porcelain boat placed behind the filled portion of the catalyst in the decomposition tube and, being taken out cautiously from the latter before entering into the analysis, is placed on the material in the boat. When the decomposition of the material is completed, the boat and the catalyst are introduced together into the decomposition flask and the process of the analysis is conducted as mentioned above.

In the case of analysing volatile liquids (for example carbon bisulphide and thiophen in the following table) a small tube of about 5 mm. wide and of about 20 mm. long provided with a comparatively long neck of about 2 mm. wide and of about 30 mm. long is prepared and, in order to introduce a small drop of the material to be analysed into the bottom of the tube, a capillary is used, of about 1 mm. diameter, which is drawn out at one end for some millimeters to the thickness of a hair. By this means one can avoid putting the material on the wall of the weighing tube. After weighing the material in this tube, some benzene is added by means of another capillary, and a small capillary (Fig. 2), sealed at the upper end, which prevents superheating by producing a slow stream of air bubbles through the liquid, is immersed in it. The benzene freezes when cooled by ice and enables one to avoid the loss by vaporization and easily to charge the tube into the apparatus which is sealed afterwards and, being heated in a bath at a suitable temperature, serves to control the desired vapour velocity of the material (Fig. 2). In the same way it is able to determine even a trace of sulphur compound in a very large quantities of organic liquids, only by using a larger weighing tube and the suitable outer apparatus (Fig. 2).

Materials	<i>P</i> (mg.)	<i>a</i> (gr.)	<i>T</i> ₁ (c.c.)	<i>T</i> ₂ (c.c.)	% of S. calc.	% of S. found
Carbon bisulphide,* CS ₂	4.62	0.03375	25.66	13.20	84.24	84.64
Thiophen, C ₄ H ₄ S	15.98	0.05027	36.50	18.00	38.14	38.13
Thioacetic acid, CH ₃ COSH	8.55	0.03375	5.09	2.83	42.14	41.93
Phenyl thiocyanate, C ₆ H ₅ NCS	10.65	0.03745	24.90	17.95	23.73	23.49
Ethyl benzene sulphonate, C ₆ H ₅ SO ₃ C ₂ H ₅	10.31	0.03894	23.95	19.39	17.23	17.20
Ammonium bromocamphor sulphon- ate, C ₁₀ H ₁₈ O ₄ NBrS	12.30	0.03837	22.62	19.47	10.08	10.40
Barium benzene sulphonate, (C ₆ H ₅ SO ₃)Ba + H ₂ O	13.95	0.03837	22.92	18.40	12.66	12.98
Quinine sulphate (C ₂₀ H ₂₄ N ₂ O ₂) ₂ SO ₄ H ₂ + 8 H ₂ O	6.43	0.03745	22.64	22.03	3.60	3.75
Thialdin, $\begin{array}{c} \text{CH}_3 \cdot \text{CH} \begin{array}{l} \text{S} \cdot \text{CH}(\text{CH}_3) \\ \text{S} \cdot \text{CH}(\text{CH}_3) \end{array} \text{NH} \end{array}$	6.73	0.03745	22.51	15.80	39.29	39.57
Thiodiphenylamine, $\begin{array}{c} \text{C}_6\text{H}_5 \begin{array}{l} \text{S} \\ \text{NH} \end{array} \text{C}_6\text{H}_5 \end{array}$	9.59	0.03837	22.76	18.97	16.10	15.95

* It was informed by Prof. P. Sabatier (*Bull. Soc. Chim.*, [4], 15 (1914), 228) that the carbon bisulphide was reduced by means of hydrogen on nickel catalyst and gave rise to the formation of CH₂SH)₂, but in our experiment it was not observed while the most active part of the catalyst existed.

Summary.

A microanalytical determination of sulphur in organic compounds is carried out by decomposing cautiously the material to be analysed in the hydrogen atmosphere on reduced nickel, which absorbs the sulphur completely and changes itself into sulphide, and by determining iodometrically the hydrogen sulphide which is evolved from the reduced nickel when it is dissolved in hydrochloric acid. It was found thus that the nickel catalyst is able to be applied to the organic microanalysis of sulphur.

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COLORIMETRIC DETERMINATION OF SULPHURIC ACID.

By Junzô YAMAZAKI.

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In the benzidine method of volumetric determination of sulphuric acid, we precipitate the acid as benzidine sulphate by means of benzidine hydrochloride and titrate the precipitate directly by alkali. We may also determine the acid by the estimation of benzidine in the precipitate⁽¹⁾; similarly, when the amount of benzidine hydrochloride added is known, we can reckon the acid by estimating the residual benzidine in solution. Moreover, if benzidine can be estimated colorimetrically, the estimation of the acid may be simplified and be useful for some purposes.

A search for the reagent which will give a quantitative colouration with benzidine, has shown that furfural is the most convenient and handy one among a good deal of varieties of chemicals for that purpose. The conditions and properties of this colouration were as follows:—

1. In the presence of small amounts of HCl and ethyl alcohol, aqueous solution of benzidine hydrochloride forms a canary yellow solution with furfural at room temperature. The colour hardly changes its intensity on standing.

2. When the equal amounts of furfural in large excess are added to the increasing amounts of benzidine, the depths of colouration produced are proportional to the amounts of benzidine.

Thus, 5 c.c. of benzidine hydrochloride solutions of the concentrations of 6 : 5 : 4 : 3 (6 = 0.006 mg. mol. per 5 c. c.) are mixed with 0.2 mg. mol. of furfural. The relative depths of colouration are measured, comparing the neighbouring two liquids in a colorimeter.⁽²⁾ The depths of colouration are found to be proportional to the concentration of benzidine hydrochloride (Tab. 1). This holds also in higher and lower concentrations of benzidine.

TABLE 1.

Concentration of benzidine solutions	6	:	5	:	4	:	3
Ratio of concentrations	1.20		1.25		1.33		
Ratio of depths of colouration observed	1.19		1.25		1.33		

(1) Raiziss and Dubin, *J. Biol. Chem.*, **18** (1914), 297; Pezzi, *Giorn. chim. ind. applicata.*, **3**, 10 (*Chem. Zentr.*, 1921, II, 715).

(2) Colorimeter-nephelometer by Baudouin and Benard, Pellin et Cie., Paris, was used.

3. When the increasing amounts of furfural are added to the equal amounts of benzidine hydrochloride, the colourations produced are not constant, but increase with the amount of furfural as shown in Fig. 1.

4. Increase of acidity of the mixture somewhat deepens the colouration.

The above results show that when benzidine hydrochloride is submitted to colorimetry, the equal amounts of furfural (excess to benzidine) must be added to the comparing solutions of the same acidity.

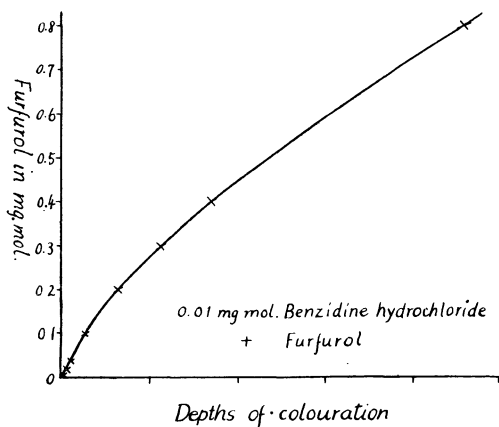


Fig. 1.

Ordinary Method.

Pure ammonium sulphate solution of the concentration of 4–5 millimols is prepared for standard solution. The concentration of the test solution should be nearly equal to this. To 5 c. c. of both solutions taken in large test-tubes (Fig. 2, B) add 2 drops of brom-phenol-blue (0.04%), and *N*-HCl until the indicator turns perfectly yellow, and then 5 c.c. of water respectively. Two c.c. of *M*/20 benzidine hydrochloride are next added, drop by drop, to each tube, followed by 5 c.c. of 90% acetone to complete the precipitation. After standing 10 minutes, the solutions are filtered by a filtering apparatus.

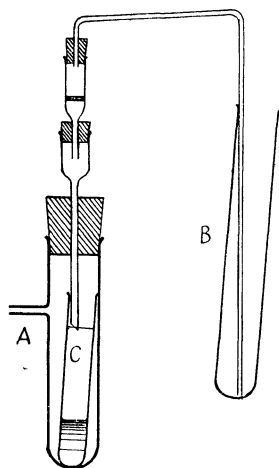


Fig. 2.

As shown in Fig. 2, the filtering apparatus is like that of Pregl's in the determination of halogens, provided that the "glass filter" (Pattern 12 G 2/<7, Schott & Gen, Jena) is preferably used in the place of "Filterröhrchen". By a gentle suction from A, the precipitates are all brought into the filter, where it is washed 3 times by 2 c.c. of 90% acetone and finally once by 3 c.c. of it. When all acetone has gone through the filter, it is sucked strongly for a few minutes to dry up any wash liquid left in the filter. The suction is then stopped, the filtrate in A is poured

out and in that place a clean test-tube with a mark at 20 c.c. (Fig. 2, C) is settled. Fifteen c.c. of a mixture of absolute alcohol and *N*/10 NaOH (1:1 by volume) are taken into the tube formerly used for the precipitation and are shaken to dissolve any benzidine sulphate adhered to the wall of the vessel. Then, the solution is sucked into the filter, which dissolves the precipitate and gathers into the test-tube.

This operation is performed twice with both solutions at a single apparatus or at the same time by a pair of apparatuses, which may save time. The two solutions collected under the filter are then taken out, added by 10 drops of 10% BaCl₂, 1 drop of phenolphthalein and with gentle agitation *N*-HCl drop by drop, until the alkaline reaction fades, and 10–15 drops furthermore. Fill the tubes up to the mark, mix well and pipette out 5 c.c. from each solution into a pair of clean test-tubes. To them add 2 c.c. of 1% furfural aq. and put the resulting coloured liquids to a colorimeter. It takes about 2 hours for the operation. The solution before adding furfural can be preserved unchanged for days. It is advisable to use sky-blue glasses on the eye-piece of a colorimeter; they facilitate the comparison well.

For the furfural solution, freshly distilled furfural should be used. The pale yellow colour of the solution does no harm on the comparison. Also commercial furfural can be used, when it is decolourized by animal charcoal in aqueous solution. In this case, the concentration of furfural is somewhat lowered.

In comparing two ammonium sulphate solutions (0.050 and 0.025 mg. mol. per 5 c.c.) by this method, the result obtained was 2:0.99, showing that the sulphate was quantitatively derived into coloured substances.

Application to urine analysis. The sulphates in urine are determined after the accompanying phosphate is removed by the method of Fiske⁽¹⁾ as follows. Into a 100 c.c. volumetric flask sufficient urine to contain 40–50 mg. H₂SO₄ in the form of inorganic sulphate (ordinarily, an amount of urine corresponding to a 30-minute period will be suitable) is introduced and diluted to about 50 c.c. with water. A drop of phenolphthalein solution is added, followed by ammonia water until the contents become faintly pink. Now add about 1.5 gr. of finely powdered basic magnesium carbonate, make up to the mark, shake for a minute and let it stand for 30 minutes. In case of foaming, a drop of caprylic alcohol facilitates to make up to the mark exactly. In accurate work, the volume of carbonate should be taken into calculation (about 0.8 c.c.). The mixture is filtered through a dry paper into a dry flask. This filtrate is used for the following two determinations.

Inorganic sulphate. Five c.c. of the filtrate are directly proceeded as above.

(1) *J. Biol. Chem.*, **47** (1921), 62.

Total sulphate. Five c.c. of the filtrate are pipetted into a test-tube, to which 0.5 c.c. conc. HCl is added, and the tube is dipped into vigorously boiling water for 30 minutes. The hydrolysed brown liquid is then poured into a small dish with the aid of small amount of water. The contents of the dish are evaporated on a water bath to perfect dryness and laid heated 10 minutes longer. The residue is extracted with 10 c.c. of hot water in several times, transferred into a precipitation tube and treated as before, provided that there is no need of adding 5 c.c. of water before the precipitation with benzidine hydrochloride.

Results. Two samples of normal urine are taken and their contents of sulphates are determined both by gravimetric and colorimetric methods to compare results.

TABLE 2.

Urine No.	d_{15}°	Cl present at the time of precipitation mg.	Inorganic sulphate SO_3 . mg./c.c. urine		Total sulphate SO_3 . mg./c.c. urine	
			gravimetric	colorimetric	gravimetric	colorimetric
I	1.024	6.4	1.614	1.61		
		221*			1.90	1.56
II	1.030	11.0	2.121	2.14		
		8.5			2.265	2.23

* HCl for hydrolysis was neutralized, not evaporated off.

As seen from the table, when there is a large amount of chloride present in the sample, it gives bad results. This is why in total sulphate estimation the hydrolysing HCl must be removed by evaporation.

Rapid Method.

When the testing solution is colourless, or can be made colourless, we can determine its sulphuric acid in estimating the residual benzidine in solution colorimetrically, after the precipitation of sulphuric acid by benzidine. In such a case, the estimation is very simple.

Five c.c. of the standard (0.01 mg. mol. $(\text{NH}_4)_2\text{SO}_4$ per 5 c.c.) and testing solutions are taken into a pair of centrifugal tubes, and each solution is acidified with 5 drops of *N*-HCl. To them add 2 c.c. of benzidine hydrochloride solution (0.03 mg. mol. per 2 c.c., accurately) followed by 2 c.c. of 1% furfural solution respectively. After careful mixing, the solutions are centrifuged and the supernatant clear liquids are put to colorimeter.

In the case when more concentrated sample can be obtained, the following recipe is advantageous: 5 c.c. of the standard (0.025 mg. mol. $(\text{NH}_4)_2\text{SO}_4$

per 5 c.c.) and testing solutions, 5 drops of *N*-HCl, 5 c.c. of benzidine hydrochloride (0.075 mg. mol. per 5 c.c.) and 5 c.c. of furfural solution respectively.

Of course the above performance can be applied to any other proportion of reagents and sample, but always the benzidine reagent must not be added too excessively, for it brings the ratio of residual benzidine in two solutions near to 1, and it requires to observe the ratio of the two more accurately, which is not advantageous for the colorimetry. About 3 times excessive amount of benzidine reagent is suitable.

Preparation of solutions. *Standard solution.* 0.1320 Gr. (for the first recipe) or 0.3300 gr. (for the second) of pure ammonium sulphate is dissolved in water and made up to 500 c.c.

Benzidine solution. The solution of benzidine in dilute HCl is heated with small amount of animal charcoal and filtered. To the filtrate conc. HCl is added, until the white precipitate ceases to separate, which is soon collected by a centrifuge and dissolved in hot water. The solution is filtered hot into a pure NaOH solution and after the mixture has cooled, the precipitated benzidine is taken on a filter, washed by water, recrystallized from a large amount of water and dried in air oven. 1.380 Gr. of this purified benzidine is dissolved in water with 36 c.c. *N*-HCl and made up to 500 c.c. This solution is colourless and can be kept long without deterioration.

Calculation. Standard solution containing a mg. mol. sulphate and testing solution containing x mg. mol. sulphate in equal volume are mixed with b mg. mol. benzidine hydrochloride respectively. There remains $b-a$ and $b-x$ mg. mol. benzidine hydrochloride in solutions after the precipitation. Furfural solution is added to each solution and the colouration that is proportional to residual benzidine is produced. Let the layers of these liquids giving the same intensity of colour be s and s_x . Then,

$$s(b-a) = s_x(b-x), \text{ or } x = b - (b-a) \frac{s}{s_x}.$$

In the first instance of the above recipes, $x = 0.03 - 0.02 \frac{s}{s_x}$.

In the second instance, $x = 0.075 - 0.050 \frac{s}{s_x}$.

This method gives high results in the presence of phosphate and low results in the presence of chloride (Tab. 3). It is necessary to remove phosphate when this is present over 5 times (in mol) excess to sulphate.

The effect of chloride can be partly decreased by the use of more concentrated sample and benzidine solutions. But by the use of a standard solution containing approximately equal amount of chloride, the most of the effect can be canceled. The method is, therefore, a convenient one in a routine work when the contents of chloride are approximately known.

TABLE 3.

SO ₄ mg. mol.	Cl mg. mol.	PO ₄ mg. mol.	SO ₄ found mg. mol.
0.0125	0	0	0.0125
0.0125	0	0.125	0.0128
0.0125	0.375	0	0.0113

Application to urine analysis. This method can be applied on urine after it is decolourized by animal charcoal. The charcoal should be freed from sulphate, phosphate and especially from iron, as far as possible, by digesting with hydrochloric acid and subsequent washing with water. O. Warburg's "Silicat-zuckerkohle"⁽¹⁾ well serves for this purpose, as it is free from these substances.

For inorganic sulphate, 1 gr. or less of dried charcoal is added to 20 c.c. of urine solution (phosphate removed, see page 175), and after 20 minutes the solution is filtered through a fine filter paper into a dry flask. Five c.c. of this decolourized solution is proceeded as directed above.

In case of total sulphate, 10–20 c.c. of urine solution are hydrolysed in a large test-tube with its 1/10 volume of conc. HCl as directed in ordinary method. The residue is extracted with hot water, the extract is diluted to a definite volume (say, 20 c.c.), and is decolourized by a small amount (0.2–0.5 gr.) of animal charcoal. Five c.c. of this solution are proceeded as previously noted.

Standard solution. The injurious effect of chloride originally present in urine (see Urine III, Tab. 4) can be eliminated by the addition of sodium chloride to the standard solution. 0.1320 Gr. recrystallized ammonium sulphate and 1.2 gr. sodium chloride are dissolved in water and made up to 500 c.c. The solution serves as a standard for these estimations and gave following results.

(1) *Biochem. Z.*, 145 (1924), 473.

TABLE 4.

Urine No.	d_{15}^4	Cl present at the time of precipitation. mg.	Inorganic sulphate SO_3 . mg.		Total sulphate SO_3 . mg.		Remarks	
			gravi-metric	colori-metric	gravi-metric	colori-metric	Standard solution used	Preservative added
III	1.016	7.58	0.816	0.77			$(\text{NH}_4)_2\text{SO}_4$ 0.01 mg. mol. per 5 c.c.	Toluol
		—			0.904	0.91		
V	1.024	6.73	2.130	2.10			$(\text{NH}_4)_2\text{SO}_4$ 0.0125 } per 5 c.c. NaCl 0.20	"
		13.1			2.283	2.31		
VI	1.016	8.91	0.835	0.82			$(\text{NH}_4)_2\text{SO}_4$ 0.025 } per 5 c.c. NaCl 0.40	Phenol
		17.8			0.927	0.93		
VII	1.028	9.70	2.228	2.23			"	—
		19.0			2.368	2.37		

Remarks.

The main parts of these methods lie in the precipitation of benzidine sulphate and colorimetry, and especially for the former performance; the following precautions are necessary: Sulphate is precipitated in slightly acidic solution, containing less than 5 times (in mol) of phosphate or 5 times of chloride (the effect of chloride is smaller in ordinary method than in rapid method). In the presence of other acid radicals which form difficultly soluble salts with benzidine or any oxidizing agent which attacks benzidine, the methods are not applicable.

Summary.

1. Sulphate is precipitated by benzidine hydrochloride and on resulting precipitate of filtrate the amount of benzidine is determined colorimetrically. From that value, the amount of sulphate is calculated.
2. "Rapid method" is given, which is simple in execution and does not take much time. The purification of benzidine for this method is also given.
3. The methods are applied on urine analyses and seem to be useful especially in clinical works.
4. In ordinary method 2–2.5 mg. H_2SO_4 per 10 c.c. can be determined; in rapid method 1–1.5 mg. per 5 c.c. is necessary.
5. When any hindering substances are absent, the accuracy of the results always lies within the range of accuracy of colorimetry.

In conclusion, the author wishes to express his sincere thanks to Prof. T. Soda for his kind guidance during the work.

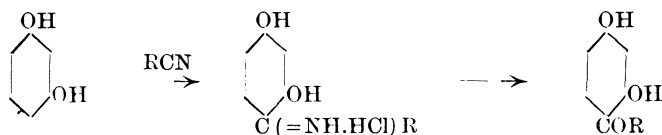
Chemical Institute, Faculty of Science,
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THE APPLICATION OF THE HOESCH REACTION TO NITROBENZONITRILES.

By **Masataro YAMASHITA.**

Received June 16, 1928. Published July 28, 1928.

Since Hoesch⁽¹⁾ synthesised various aromatic hydroxy-ketones from nitriles and certain phenols in the presence of anhydrous zinc chloride and dry hydrogen chloride, as indicated in the following scheme:—



this reactions has been applied extensively in the preparation of various aromatic carbonyl compounds. So far as I am aware, this reaction has not yet been applied to the aromatic nitriles containing a nitro-group. The synthesis of such compounds seems interesting in that the resulting compounds might be used for the preparation of the derivatives of benzophenone having various substituents in the benzene nucleus, by converting these compounds into the corresponding amino-derivatives, and then diazotising the latter. When the condensation was over and the reduction of the condensation products was in progress, Korezynski and Nowakowski⁽²⁾ had recently published the synthesis of *p*-nitrobenzoresorcinol and *p*-nitrobenzophloroglucinol for another purpose. Accordingly, the results already obtained are published in the present communication.

The present author attempted to condense resorcinol or phloroglucinol with *o*-, *m*-, and *p*-nitrobenzonitriles by the Hoesch reaction. Whilst *o*-nitrobenzonitrile did not react with resorcinol or with phloroglucinol, *m*- and *p*-nitrobenzonitriles condensed to yield the nitro-derivatives of benzophenones. The yield of the derivative of phloroglucinol was much better than that of the corresponding derivative of resorcinol.

The reduction of the condensation products is now in progress.

(1) *Ber.*, **48** (1915), 1122.

(2) *Bull. Soc. Chim.*, 4 série, **43** (1928), 327.

Experimental.

In order to improve the yield of the condensation product of resorcinol with *m*- or *p*-nitrobenzonitrile, the quantity of the components was first varied and the following were found to be the best for the purpose.

4'-Nitro-2:4-dihydroxybenzophenone, $(\text{NO}_2)\text{C}_6\text{H}_4\text{COC}_6\text{H}_3(\text{OH})_2$. Three grams of *p*-nitrobenzonitrile and 2.5 grams of resorcinol were dissolved in 150 c.c. of absolute ether, and, after adding two grams of freshly fused and powdered zinc chloride, a gentle stream of dry hydrogen chloride was passed into the solution for five hours at room temperature, when a brownish red oil separated. After allowing the solution to remain overnight and decanting the ether, the oil was washed with ether in order to remove the unchanged *p*-nitrobenzonitrile, and boiled with 50 c.c. of water for half an hour. As the crystals thus separated were contaminated with tarry matter, they were freed from the latter by collecting them while still hot. The yield of the crude product amounted to 0.9 gram. After being recrystallised from dilute alcohol, they separated in pale yellow crystals melting at 203° (Found: C=60.29; H=3.59; N=5.97; Mol. wt., by the Rast method, 267. $\text{C}_{13}\text{H}_9\text{O}_5\text{N}$ requires C=60.23; H=3.50; N=6.00%. Mol. wt., 259.1).

Korezynski and Nowakowski⁽¹⁾ gave 200° as its melting point.

The Methyl Derivative, $(\text{NO}_2)\text{C}_6\text{H}_4\text{COC}_6\text{H}_3(\text{OCH}_3)_2$. *4'-Nitro-2:4-dihydroxybenzophenone* (0.2 gram) was dissolved in 6 c.c. of a 10 per cent solution of sodium hydroxide and shaken with 1 c.c. of methyl sulphate for an hour, when a brownish compound (0.1 gram) separated. It crystallised from a mixture of ether and petroleum ether in pale yellow crystals, m.p. $123\text{--}124^\circ$ (Found: C=62.52; H=4.65. $\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}$ requires C=62.71; H=4.56%).

3'-Nitro-2:4-dihydroxybenzophenone, $(\text{NO}_2)\text{C}_6\text{H}_4\text{COC}_6\text{H}_3(\text{OH})_2$. Three grams of *m*-nitrobenzonitrile and 2.5 grams of resorcinol were dissolved in 100 c.c. of absolute ether, and, after adding 3 grams of freshly fused and powdered zinc chloride, dry hydrogen chloride was gently passed into the solution for five hours at room temperature, as in the preparation of *4'-nitro-2:4-dihydroxybenzophenone*, when a reddish brown oil was deposited. After allowing it to stand overnight and decanting the ether, the oil was washed with ether, and boiled with 50 c.c. of water for half an hour, when brownish yellow crystals were obtained. In order to remove tarry matter, the crystals were collected while still hot. The yield of the crude product amounted to 0.6 gram. After being recrystallised from dilute alcohol, they separated in yellow needles melting at 228° (Found: C=60.34; H=3.72; N=6.02. $\text{C}_{13}\text{H}_9\text{O}_5\text{N}$ requires C=60.23; H=3.50; N=6.00%).

(1) loc. cit., p. 333.

The Methyl Derivative, $(\text{NO}_2)\text{C}_6\text{H}_4\text{COC}_6\text{H}_3(\text{OCH}_3)_2$. 3'-Nitro-2:4-dihydroxybenzophenone (0.5 gram) was dissolved in 6 c.c. of a 10 per cent solution of sodium hydroxide and shaken with 1 c.c. of methyl sulphate for an hour, when colourless crystals were deposited. After recrystallisation from alcohol several times, they melted at 116–117° (Found: C=62.82; H=4.61. $\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}$ requires C=62.71; H=4.56%).

4'-Nitro-2:4:6-trihydroxybenzophenone, $(\text{NO}_2)\text{C}_6\text{H}_4\text{COC}_6\text{H}_2(\text{OH})_3$. One gram of freshly fused and powdered zinc chloride was added to a solution of 2 grams of *p*-nitrobenzonitrile and 1.8 grams of phloroglucinol in 100 c.c. of absolute ether, and a gentle stream of dry hydrogen chloride was passed into the solution for four hours at room temperature, when a reddish brown oil was separated. The oil was boiled for half an hour with 100 c.c. of water and the faint, yellow crystals which separated were collected and recrystallised from dilute alcohol. The gamboge yellow crystals thus obtained melted at 246–247° (Found: C=56.52; H=3.52; N=4.87. $\text{C}_{13}\text{H}_9\text{O}_6\text{N}$ requires C=56.71; H=3.30; N=5.10%).

Korczynski and Nowakowski⁽¹⁾ gave 244–245° as its melting point.

3'-Nitro-2:4:6-trihydroxybenzophenone, $(\text{NO}_2)\text{C}_6\text{H}_4\text{COC}_6\text{H}_2(\text{OH})_3$. One and a half grams of freshly fused and powdered zinc chloride were added to a solution of four grams of *m*-nitrobenzonitrile and 3.6 grams of phloroglucinol in 250 c.c. of absolute ether, and a current of dry hydrogen chloride was then gently passed into the solution for six hours at room temperature. After being allowed to stand overnight, the product was freed from the unchanged nitrile, by decanting the ether and washing it several times with ether, and then decomposed by boiling with 100 c.c. of water for half an hour, or by dissolving it in 100 c.c. of 2*N*- H_2SO_4 and subsequent boiling for half an hour. The yellow crystals thus separated were recrystallised from water, when they crystallised in faint, yellow needles melting at 194° (Found: C=56.44; H=3.40; N=5.05. $\text{C}_{13}\text{H}_9\text{O}_6\text{N}$ requires C=56.71; H=3.30; N=5.10%).

Attempts to condense *o*-nitrobenzonitrile with resorcinol or with phloroglucinol under various conditions were made, but without success, the unchanged nitrile being always recovered.

In conclusion, the author wishes to express his hearty thanks to Professor Hiroshi Nomura for his kind guidance and encouragement during this investigation.

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(1) loc. cit., p. 334.

PERMEABILITIES OF COLLOIDAL SUBSTANCES TO GASES.

By Kazuo KANATA.

Received June 19, 1928. Published August 28, 1928.

It is a well known fact that almost all amorphous substances, especially colloidal substances, absorb various gases, but the mechanism is not yet clear. The India rubber, for example, is permeable to various gases⁽¹⁾. In the present experiment it has been examined whether other colloidal substances are also permeable for gases or not, and hence whether their sorption is an adsorption phenomenon or not. The author wishes, also, to discuss on the mechanism of the permeability and absorption.

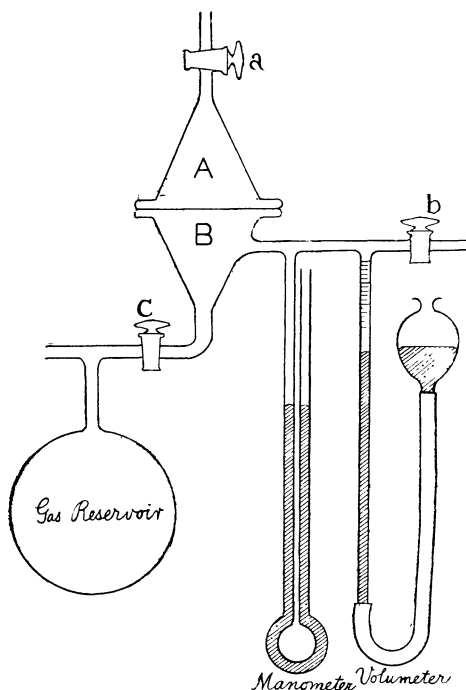


Fig. 1.

Experimentals. The apparatus used in this experiment is shown in Fig. 1. The membrane of the colloidal substance to be examined is placed between A and B. The stop-cocks a and b are opened and the air exist in the vessel and some gases which may be sorped in the mass of the membrane are exhausted by a pump. Then the cocks a and b are closed, and the gas under examination is introduced into B through the cock c. The volume change of the gas is measured with a volumeter.

The membranes used were of rubber, celluloid and geletine, while the gas tested were hydrogen, oxygen, carbon dioxide, sulphur dioxide and ammonia. For the first several hours, before the stationary state is reached, the effect of absorption is very large. The data shown in the following tables were obtained.

- (1) Graham, *J. Chem. Soc.*, **20** (1867), 235; Wroblewski, *Ann. Physik*, **8** (1879), 29; Hüfner, *Ann. Phys. u. Chem.*, **34** (1886), 1; Edwards and Pickering, *Chem. Met. Eng.*, **23** (1920), 17; Daynes, *Proc. Roy. Soc. (London)*, **97** A (1920), 286; Venable and Fuwa, *Ind. Eng. Chem.*, **14** (1922), 139.

TABLE 1.
Celluloid.

Oxygen		Hydrogen		Carbon dioxide		Ammonia	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
5	0.32	10	0.40	9	1.14	8	9.46
10	0.48	20	0.72	19	1.90	16	16.45
20	0.68	30	0.92	29	2.52	26	22.80
30	0.80	40	1.26	59	3.72	38	28.25
50	1.20	60	1.72	99	5.18	44	36.97
81	1.34	90	2.39	119	5.64	65	41.37
120	1.67	120	3.10	149	6.57	90	47.62
180	1.97	180	4.36	179	7.43	120	57.61
251	2.40	240	5.74	239	9.24	150	69.07
307	2.47	300	7.18	310	11.37	180	75.10
371	2.70	365	8.40	370	13.11	233	92.00
428	2.86	420	9.57	430	14.80	290	104.91
480	3.06					345	115.37
						413	129.34

These data are depicted in Fig. 2.

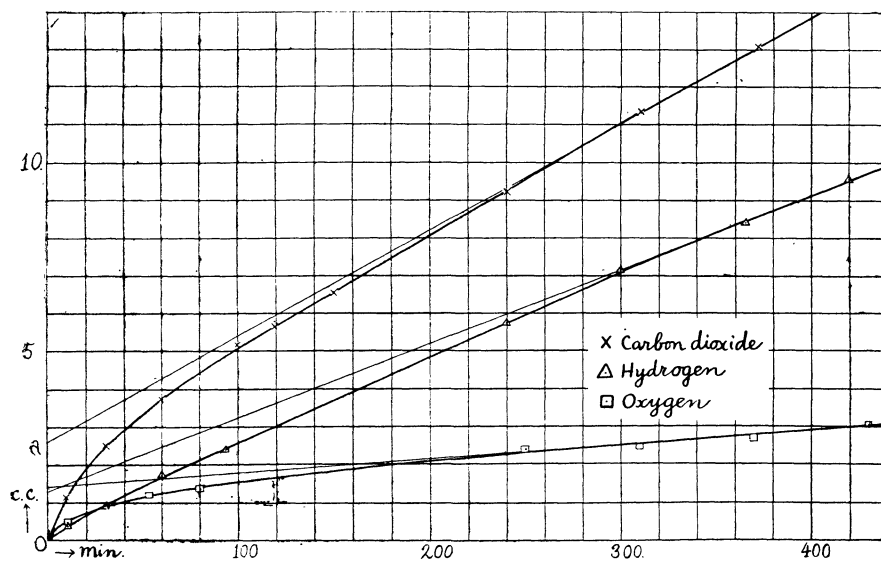


Fig. 2.

TABLE 2.

Rubber.

Oxygen		Hydrogen		Carbon dioxide		Sulphur dioxide		Ammonia	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
10	0.04	5	0.133	5	0.58	13	18.57	8	10.83
20	0.05	10	0.185	10	0.86	22	26.50	17	19.46
50	0.17	20	0.230	20	1.357	32	33.59	28	27.32
110	0.33	30	0.285	31	1.76	42	37.78	40	35.59
240	0.78	40	0.385	40	2.16	50	43.40	48	40.02
300	0.91	50	0.44	50	2.49	60	47.36	58	45.77
367	0.99	60	0.472	60	2.80	90	57.63	90	61.54
436	1.08	90	0.617	90	3.57	120	65.56	150	88.36
1372	2.95	120	0.887	120	4.29	180	78.03	200	106.34
		180	1.219	180	5.66	240	88.43	310	137.50
		240	1.503	240	6.633	300	97.00	410	165.43
		300	1.875	300	7.954	360	105.97	530	192.34
				423	10.23	422	114.45		

(The measurements on the ammonia and the sulphur dioxide have been suspended after the time shown in the bottom line of the table until the stationary state was reached.)

TABLE 3.

Gelatine.

Oxygen		Carbon dioxide		Sulphur dioxide	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
5	0.06	5	0.058	10	0.55
10	0.11	10	0.162	20	1.09
21	0.16	20	0.235	30	1.35
30	0.19	30	0.254	40	1.62
40	0.22	60	0.402	50	1.90
50	0.30	120	0.556	55	1.98
60	0.36	180	0.664	85	2.58
133	0.43	240	0.78	175	3.68
421	0.64	360	0.79	235	4.28
1375	0.815	450	0.85	295	4.82
		1410	1.328	355	5.24
				445	5.82

(The measurement on the ammonia was done only after the stationary state was reached.)

We must, therefore, continue the experiment until the volume change becomes constant, and then determine the permeability by dividing the volume change by the time interval. The relative permeabilities to the various gases are shown in the following table. (in the case of rubber, permeability to hydrogen has been taken as unity; but in other cases, oxygen as unity.)

TABLE 4.

Gas \ Membrane	Celluloid	Rubber	Gelatine	Viscosity coeff. of gas at 20°C.	Square root of gas density
Hydrogen	2.60	1.00	less than 1.00	930×10^{-7}	1.41
Oxygen	1.00	0.35	1.00	2120×10^{-7}	5.66
Carbon dioxide	8.76	3.17	4.13	1600×10^{-7}	6.63
Sulphur dioxide	—	7.90	31.90	1380×10^{-7}	8.00
Ammonia	62.3	11.4	95.2	1080×10^{-7}	4.12

Theoretical Considerations. As it became clear that these substances are permeable to gases, there is no doubt that the sorption of various colloidal substances is not an adsorption phenomenon, that is condensation of the gaseous molecules on the surface of the substance only. It will, then, be discussed something about the mechanism of the absorption judging from the present experiments. For the passability of the gas through the membrane two causes can be considered, namely the passing of gas through the pores of the substance and the dissolution.

Pass through the Pores of the Membrane. As for the porosity of the colloidal substance many authors have discussed for long time. If we assume the permeability is due to the porosity, we have to consider two cases, namely, the viscosity flow and the molecular flow.

In the case of the viscosity flow, the rate of permeabilities for various gases will be inversely proportional to the viscosities of gases, as shown in the following well known equation.

$$q = \frac{\pi r^4 (p_0 - p) t}{8 \eta l}$$

where q denotes the mass of the gas which pass through the unit area of the membrane and η , the viscosity coefficient of the gas. The viscosity coefficients of the gases are shown in the 5th column of Table 4.⁽¹⁾ Thus ammonia is more viscous than hydrogen, while the former is far more passable through membranes than the latter. It is known, therefore, that the viscosity flow is not the main cause of the permeability.

(1) Landolt-Börnstein, "Physikalisch-chemische Tabellen", 5 ed.

If the radius of pores is very small and the mean free path of the molecules is not negligible compared with the radius of pores it is the case of the molecular flow, and the permeability is inversely proportional to the square root of the density of gas.⁽¹⁾ But such a relation does not exist as shown in Table 4.

Dissolution. As has been discussed above, it is not quite plausible to assume that the permeability is due to the porosity. I think it is due to the solubilities of the gases into the membranes, and this idea is supported by many other facts. For example, the order of the solubilities of gases in these substances are almost the same as those in other substances like water. The gases of lower polarity is dissolved less while those of higher dissolved much. By the aid of the Fick's law the dissolution theory can also explain the fact that the orders of permeabilities are inverse to those of absorption in some cases.

From the Fick's law,

$$\frac{d q}{d t} = -D \frac{d y}{d x}$$

where y denotes the concentration at x , we have the following equation by using the Fourier's expansion,

$$y = y_1 + (y_2 - y_1) \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{y_2 \cos \frac{n \pi}{l} - y_1 \sin \frac{n \pi}{l}}{n} x. e^{-D n^2 \pi^2 t / l^2}$$

In the present experiment,

$$y_1 = 0 \quad \text{at} \quad x = 0.$$

By the Henry's law we have the following condition,

$$y_2 = A p \quad \text{at} \quad x = l$$

where A is the absorption coefficient.

We obtain, therefore,

$$q = \frac{D A p}{l} \left[t + 2 \sum_{n=1}^{\infty} \frac{l^2}{D n^2 \pi^2} (1 - e^{-D n^2 \pi^2 t / l^2}) \right]$$

and when t is large this equation takes the form,

$$q \approx \frac{D A p}{l} \left(t + \frac{l^2}{3 D} \right)$$

In this equation the first term $D A p t / l$ is the quantity of the gas which passes through the membrane after the stationary state has been reached. From this it can be understood that the permeability is related to both the

(1) Loeb, "Kinetic theory of gases", p. 252.

absorption coefficient (A) and the diffusion coefficient (D). Therefore, if D is very large or very small compared with A , the orders of the permeabilities are not the same as those of the absorption. The second term $Ap^{1/3}$ corresponds to Oa in Fig. 2.

From the present experiments it cannot be judged whether the dissolution is a purely physical phenomenon or the chemical changes occur at the same time. But, in the case of the rubber it has been shown by Edwards and Pickering⁽¹⁾ that the solubility of sulphur dioxide is greater than that of ammonia. On the contrary, in the ordinary solvent, the solubility of ammonia is greater than that of sulphur dioxide. It is probable that there occurs some chemical change in this case. In the case of ammonia through celluloid, after putting the membrane in the atmosphere of ammonia for a long time, the permeability increased as much as five times in comparison with the data shown in Table 4—0.2056 c.c. per min. in the experiment from which Table 4 was obtained, while 1.110 c.c. per min. after putting it in the atmosphere of ammonia for about four days—and the colour changed from white to yellow and increased transparency. Such effects also might be due to the chemical change. I think that it may be due to the chemical change in the most cases where the ammonia is dissolved much in solvent.

Summary.

1. Permeabilities of rubber, gelatine and celluloid for oxygen, hydrogen, carbon dioxide, sulphur dioxide, and ammonia were determined.
2. By ascertaining the permeabilities of celluloid and gelatine, it became clear that the sorptions of these substances are not adsorption phenomena.
3. Something about the mechanism of permeability and absorption was discussed and the author reached the conclusion that the permeability and hence the absorption is caused by the dissolution of gas in the colloidal substance.

In conclusion I wish to express my sincere thanks to Prof. J. Sameshima for his kind guidance during this experiment.

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(1) Loc. cit.

THE EFFECT OF GELATINE ON THE POLYMORPHIC TRANSFORMATION OF MERCURIC IODIDE.

By Jitsusaburo SAMESHIMA.

Received June 25, 1928. Published August 28, 1928.

The author studied the effect of various colloidal substances on the formation of mercuric iodide from mercuric chloride and potassium iodide solutions.⁽¹⁾ In the present note the effects of gelatine on the transition between red and yellow modifications of mercuric iodide are described.

The mercuric iodide was prepared from the equivalent quantities of the solutions of mercuric chloride and potassium iodide, and then it was washed with water and dried. About 0.5 gram of gelatine was dissolved in a few cubic centimetre of hot water and added about 20 grams of mercuric iodide, mixed them well by grinding in a mortar. The viscid red mass thus produced was spread on a glass plate, which had previously been coated with a thin film of paraffin in order to prevent the sticking of gelatine on the surface of glass when dried. After the mass was dried, it was taken off the glass plate, and a few of the small pieces was put in a glass capillary tube.

The pure mercuric iodide powder was put in a capillary tube of the same dimensions as above. These two tubes, the one containing the gelatinized mass and the other the pure mercuric iodide, were put in a bath of the heating liquid ("liquid paraffin" was used) side by side providing a thermometer and a stirrer. Then the liquid was heated and the colour changes of the two tubes were observed.

The heating rate was about one degree per five minutes. At 125–130°C. the colour of the pure mercuric iodide began to turn yellowish, and at 132°C. it changed to yellow completely. The gelatinized mercuric iodide, however, showed no sign of colour change at this temperature and remained in red. The gelatinized one began to change its colour at about 150°C. and it turned more and more yellowish by the elevation of the temperature. At so high a temperature as 168°C. the colours of the two capillary tubes became identical.

Now the burner was turned off and the bath was left to cool. At a temperature lower than 127°C. there appeared some red spots in the pure mercuric iodide tube, and increased their areas by and by, which at last, after a few minutes, spreaded all over the mass of iodide and turned completely to red form. Yet, the gelatinized one retains its yellow colour

(1) Sameshima and Suzuki, this journal, 1 (1926), 81.

even after cooled down to the ordinary room temperature. After some times, the surface of the gelatinized yellow mass is contaminated with some red powder, which is small crystals of mercuric iodide sublimed out onto the surface from the gelatinized mass. Therefore, if the mass is taken out from the tube and broken, it can be seen that the inside of it is quite yellow. The inside of the gelatinized mass remains yellow for months after the time of heating. Thus the yellow form may remain unchange at ordinary temperature for indefinite length of time. But if we scratch the yellow part with something like a pencil knife the part immediately turns to red.

The above described phenomena may be interpreted as follows. In the present case, gelatine act as a protecting colloid in solid phase. It retards the velocities of transformations between red and yellow mercuric iodide, over and under their transition temperature 127°C . It is a general fact that, in a mean time, there may take appearance a few number of nuclei of the stable phase out of the supercooled or superheated phase. These nuclei, then, grow in their size and at last all of the mass changes to the stable phase. But if there exist the gelatine or other colloidal substances and each particles of the supercooled or superheated phase are enveloped by these colloid, then the growing of the nuclei will be hindered, even though they appeared here and there. We may say, in general, that the transition point between enantiotropic modifications will be made unsharp by the presence of the colloidal impurities, or shows hysteresis in the transition temperature. In the other hand, these phenomena may throw some light on the Smits' theory of allotropic modifications.

An interesting lecture demonstration can be performed in the following manner. One gram of gelatine is dissolved in 10 c.c. of hot water, and the solution is transferred into a mortar, add 20 grams of mercuric iodide and mix thoroughly by grinding with a pestle. The red viscid mass thus obtained is then spread by a brush on a clean glass plate to a thin layer, and dried by gently warming on a water bath. Now half a gram of gelatine is dissolved in 5 c.c. of hot water and paint it over the red coating above described. The latter treatment is necessary because it prevent the deposition of the sublimed mercuric iodide crystals on the surface of the gelatinized layer. After drying, the plate is put in an air bath and uniformly heated to about 170°C . in a draught chamber. When the plate turns to yellow completely, it is taken out from the bath and left to cool.

The yellow plate thus obtained will retains its colour for indefinite length of time. It is the protected supercooled yellow modification of mercuric iodide. Now the plate is brought before the audience, and scratch the yellow mass with the finger nail or a pencil knife. The scratched portion will immediately changes its colour to red, while the untouched

portion will remain in yellow. We can write, therefore, some letters or figures in red colour on the yellow surface.

Moreover, an interesting fact was observed. On heating the gelatinized red iodide on a desk near the window, the lighter side of the mass turns yellow first and then the darker side follows it afterward. On keeping the yellow mass near a window at the ordinary temperature, the light side of the surface contaminated firstly with the red powder of sublimed iodide, while the dark side remains yellow longer. Thus the light energy accelerate the transformation velocity of the polymorphic changes.

Summary.

The mercuric iodide containing gelatine shows hysteresis on the transition temperature, i.e. it is necessary to heat considerably higher than 127°C . to transform the red modification into the yellow one, and on the contrary, the yellow one remains unchange for indefinite length of time at the room temperature. In this case gelatine act as a protecting colloid in a solid phase.

A lecture demonstration has been described of showing the behavior of the protected supercooled mercuric iodide.

The transformation of mercuric iodide of metastable form to that of stable one is accelerated by the light energy.

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MICRO-IDENTIFICATION OF ISOMERS AND HOMOLOGUES
IN THEIR MIXTURE.

I. THREE ISOMERIC XYLENES.⁽¹⁾

By Masao MIGITA.

Received June 26, 1928. Published August 28, 1928.

Xylene occurs more or less in almost every sample of petroleum. In coal-tar it is one of the chief constituents of the "solvent naphtha", and it is contained also in raw wood-spirit. Thus xylene is very often met with in

(1) More detailed description shall be given in the Nippon Kwagaku Kwaishi in Japanese.

studies of hydrocarbons, yet satisfactory methods to identify its three isomers, *o*-, *m*- and *p*-xylenes, especially in a sample of limited quantity, could not be found in literature.

It would be proper to consider that xylene, obtained by dry distillation of natural products, is a decomposition product of more complicated substances. If we can ascertain to which of three isomers the xylene in question belongs, it would enable us to get a key to trace its origin in the mother substances. For this purpose, I have tried to detect and identify three isomeric xylenes in their mixture with the smallest quantity of the sample. Two methods, sensitive colour-reaction and observation under microscope, were tried for identification in micro-scale.

I. Colour-reaction.

Among phenomena such as oxidation, reduction, halochromy, pseudomerism, etc., which produce colour-change, pseudomerism seems to have the widest application in analytical field. Nitro-compounds often give sharp colour-reactions when they are transformed from nitro- to aci-form; detection of primary and secondary alcohols by V. Meyer's method and Liebermann's reaction for secondary amines are good examples of application of pseudomerism of nitro-derivatives.

On the colour-reactions of nitro-derivatives of aromatic hydrocarbons, Stultz⁽¹⁾ describes that alcoholic solution of trinitro-pseudo-cumene gives with a drop of caustic potash an intense green coloration which turns brown after a short time. Trinitro-*m*-xylene gives under the same condition similar colour-reaction, while 2, 4-dinitro-toluene produces a pure blue colour and 2, 4, 6-trinitro-toluene a fuchsine red. On the other hand, no colour change is observed in the case of 2, 6-dinitro-toluene and trinitro-mesitylene.

Lepsius⁽²⁾ describes also that 2, 4, 6-trinitro-toluene gives in acetone solution a bordeaux red coloration.

As no description is found about trinitro-*p*-xylene, I have prepared from pure *m*- and *p*-xylenes their trinitro-derivatives (2, 4, 6-trinitro-*m*-xylene and 2, 3, 5-trinitro-*p*-xylene), and examined their colour-reactions towards alkali in some solvents.⁽³⁾

(1) *Ber.*, **42** (1909), 3608.

(2) *Chem. Zt.*, **20** (1896), 839.

(3) As for *o*-xylene, it is known for its stability toward nitrating agent, and under the same condition in which *m*- and *p*-xylenes form trinitro-derivatives, it only forms oily lower nitro-compounds.

1. **Alcoholic solution.** With a drop of caustic potash, the *m*-compound in this solution gives instantly an intense bluish green coloration which turns on standing dull yellow, and finally a dark brown precipitate settles from the solution. In the case of the *p*-compound colour does not develop instantly, but in a few second the solution is tinged orange and then turns to a reddish brown tone, similar to that of iodine-tincture. On standing, the solution becomes turbid and a reddish brown deposit appears.

Thus we can observe remarkable differences in the two colour-reactions: (1) The colours produced by the two components form a fair contrast. (2) Both colorations do not occur simultaneously; one takes place instantly, while the other after a sufficient interval. (3) In the first the coloration fades in its tone while in the second it becomes deeper in the course of time.

From these facts we can expect that these reactions may be highly sensitive when applied to the detection of *m*- and *p*-xylenes in their mixture. In fact, when a mixture of the two alcoholic solutions above mentioned is treated with a drop of alkali, bluish green coloration appears at once, and after a short time, the reddish colour, characteristic to trinitro-*p*-xylene, predominates. The tinge of the first coloration and the time-required for appearance of the second, are variable with different proportions of the two components. The larger the quantity of the *m*-compound is, the more intense is the green coloration and the longer is the time required. For example, light green colour, which is immediately followed by the second coloration, is distinctly observed with a mixture of 2 c.c. of alcoholic solution of the *p*-compound and 0.05 c.c. of that of the *m*-compound. According to Blanksma⁽¹⁾ 100 c.c. alcohol dissolves 0.039 gr. trinitro-*m*-xylene at 20°C., consequently only 0.00002 gr. of the *m*-compound is contained in 0.05 c.c. of the alcoholic solution. The above example serves to show the sensitivity of this colour-reaction.

2. **Acetone solution.** The colours produced by the trinitro-*m*- and *p*-xylenes in this solution, with a drop of caustic alkali, are dark green and reddish brown respectively, and both colorations take place instantly, and do not change rapidly in their tones. Therefore, in case of mixture, a mixed colour is observed. For example, an acetone solution containing two trinitro-compounds in about equal proportion, takes a violet hue. On the other hand, in a mixture very rich in one of the components, the colour produced by the other can hardly be distinguished. Therefore, this reaction

(1) *Rec. trav. chim.*, 25 (1906), 177.

appears, at first sight, to be of no value for analytical purpose. Nevertheless, this colour-reaction is indispensable to detect and identify the very small quantity of *p*-xylene in a mixture rich in *m*-xylene; for acetone dissolves, even when hot, only a trace of trinitro-*m*-xylene but readily the *p*-compound. On the other hand, as the two nitro-compounds are almost equally soluble in alcohol, if the identification of the same sample is carried out in alcoholic solution, the colour produced by the *p*-compound will be ambiguous.

In conclusion, in the case of a mixture of pure isomeric xylenes we can successfully detect and identify *m*- and *p*-xylenes by colour-reactions of their trinitro-compounds either in alcoholic or in acetone solution.⁽¹⁾ But in the case of a mixture with other compounds, as is often the case, say in solvent naphtha, substances with similar colour-reactions, such as trinitro-pseudo-cumene, 2, 4-di- und 2, 4, 6-trinitro-toluene must be previously removed. This will be an easy task if we avail the small solubility of trinitro-*m*- and -*p*-xylenes in ordinary solvents, such as ether, alcohol, and acetone.

II. Microscopic Method.

An application of a polarisation microscope for identification of a very minute quantity of substances has already been recommended by Emich,⁽²⁾ Behrens,⁽³⁾ and others. In case of mixture, however, it is applicable only under the following conditions: (1) Crystals to be examined should be of different optical properties. (2) Crystals of each component should be roughly separated by some suitable solvents. This condition is necessary to raise accuracy and sensitivity of the result.

Besides, when refractive indices of a crystalline organic compound are measured by immersion-method, it must be kept in mind that organic substances, different from inorganic ones, are more or less soluble in immersion-media. And as this always causes the change of refractive indices of the media, we can not often find the true values for refractive indices of organic substances. For analytical purpose, however, accurate values for refractive indices are not necessary, and it is sufficient to find a medium which stands, with regard to refractivity, in different relations with each component of the mixture in question.

(1) Actual treatments shall be described in a later paper.

(2) Emich, "Lehrbuch der Mikrochemie", 2 Aufl. (1926), 21.

(3) Behrens-Kley, "Mikrochemische Analyse", I, 4 Aufl. (1921); "Organische Mikrochemische Analyse", 2 Aufl. (1922).

Now, to detect the three isomers of xylene under microscope, we must first obtain their crystalline derivatives. As a simple and effective method for this purpose, so-called "direct substitution" processes, nitration, bromination, and sulphonation, were tried.

1. **Esotetrabromo-compounds.** Among various brominated xylenes, esotetrabromo-xylenes are the most preferable for its easiness of formation and for having no isomers. Properties important for distinction of the three esotetrabromo-xylenes are given in Table 1.

TABLE 1.

	Esotetrabromo- <i>o</i> -xylene.	Esotetrabromo- <i>m</i> -xylene.	Esotetrabromo- <i>p</i> -xylene.
Melting point.	258°*	240°**	253°
Solubility.	Soluble in hot CHCl_3 ; sparingly in cold.	Soluble in cold CHCl_3 ; soluble in hot acetone.	A little soluble in cold CHCl_3 ; sparingly in hot acetone.
Properties of crystals. For Aniline. For $\alpha\text{-Br-C}_{10}\text{H}_7$ and CH_2I_2 .	White silky needles; extinction straight; elongation negative. $n_1 > N$.*** A little soluble. $n_2 > 1.8$.****	} The same. n_1 slightly $> N$. Readily soluble. The same.	The same. $n_1 > N$. Readily soluble. The same.

* Values reported by different observers are not same: 261° (Klages and Sommer), 254–5° (Blümlein), 260° (Jacobsen).

** 240° (Fittig and Bieber), 247° (Auwers and Kriekritz).

*** n_1 and n_2 are indices of the faster and the slower rays in a crystal respectively. Therefore, always $n_1 < n_2$. In this report N represents refractive index of the medium in question, but is not always equal to that of the pure medium.

**** As the consequence of having 4 atoms of Br in one molecule, these compounds have such extremely high refractive indices, that n_2 cannot be measured with ordinary immersion-media. This is a drawback of these compounds.

Though we have solvents to separate the three tetrabromo-compounds, their optical properties, as shown in the table, are insufficient to distinguish them. In short, they are not proper derivatives to identify three isomeric xylenes under microscope.

2. **Trinitro-compounds.** *o*-Xylene is difficulty nitrated, trinitro-*p*-xylene can not have any isomer structurally. Only *m*-xylene is capable to form three isomeric trinitro-derivatives, but as the consequence of the orienting influence of the two meta-standing methyl- and of added nitro-groups, 2, 4, 6-trinitro-*m*-xylene is the only product obtained by the direct substitution with nitrating acid. Here again, the trinitro-compounds are rather easily prepared than the lower ones. Some properties of trinitro-*m*- and -*p*-xylenes are shown in Table 2.

TABLE 2.

	2,4,6-Trinitro- <i>m</i> -xylene.	2,3,5-Trinitro- <i>p</i> -xylene.
Melting point.	179°*	137–8°
Solubility.	Very sparingly soluble in alcohol and acetone, both in hot and cold.	Very sparingly soluble in hot and cold alcohol; soluble in hot acetone.
Crystalline form, etc.,	Thin prisms or hexagonal plates, with beautiful interference colour; pale yellow.	Thick prisms; light yellow.
Optical properties.	Extinction straight; elongation positive.**	Extinction straight;*** elongation negative.
For α -Br-C ₁₀ H ₇ .	$n_1 < N < n_2$ (for prisms); $n_2 > N$ (for plates).	$n_1 > N$.

* Here again, values given by different observers are not concordant 176° (Grevingk), 177° (Luhmann), 180–1° (Knoevenagel), 182° (Tilden).

** Freshly formed crystals have elongations both positive and negative, but crystals recrystallised from alcohol have only positive elongation.

*** Trinitro-*p*-xylene crystallises in monoclinic prisms, but the cleavage being perfect toward (001), the face most frequently observed is (001) [Groth, "Chemische Krystallographie," IV, 667]. Hence nearly all crystals extinct in straight position. Very few crystals show oblique extinction. Their angle of extinction amounts about 30° [28° (Groth)].

As it is evident from the above table, the trinitro-compounds are most satisfactory derivatives for the identification of *m*- and *p*-xylenes.⁽¹⁾ Their refractive indices need not be measured. We are only to determine their signs of elongation. However, it is better to make sure of the result by determining the refractive indices.

3. Sodium salts of the sulphonic acids. Trinitro-derivatives leave little to be desired for the detection of *m*- and *p*-xylenes. But as we have not a suitable method to detect *o*-xylene, finally sulpho-derivatives were examined.

o-Xylene easily forms 4-sulphonic acid when treated with conc. sulphuric acid at 80–90°C.⁽²⁾ Under the same condition *m*-xylene forms 4- and 2-sulphonic acids, but the former in far larger quantity.⁽²⁾ *p*-Xylene-sulphonic acid is usually obtained by dissolving *p*-xylene in weak fuming sulphuric acid,⁽²⁾ and one of the technical methods to separate *p*-xylene is based on its insolubleness in ordinary conc. sulphuric acid. However, I have observed that under the above condition, it is also easily converted into 2-sulphonic acid, as Crafts⁽³⁾ has already mentioned.

(1) A sample, very rich in *m*- or *p*-xylene, can be determined simply from the observation of its nitration. When a sample is very rich in *p*-xylene, dinitro-*p*-xylenes separate out as a crystalline mass, during or after the addition of nitrating acid. In the case of a sample containing a large quantity of *m*-xylene, trinitro-*m*-xylene crystallises out in beautiful long needles from the reacting mixture, when heated in an oil bath.

(2) Jacobsen, *Ber.*, 10 (1877), 1009; 11 (1878), 22.

(3) *Z. anal. Chem.*, 32 (1893), 243.

For the purpose of identification under microscope, their barium salts were first compared. Solubility in water markedly decreases in the order of *m*-, *o*-, and *p*-derivatives, but they proved unsuitable for analytical purpose, for *o*- and *m*-compounds only form crystalline crusts, without giving well-defined crystals.

The sodium salts were next prepared from the barium salts, and their properties compared (see Table 3).

TABLE 3.

	Na <i>o</i> -xylene-4-sulphonate.	Na <i>m</i> -xylene-4-sulphonate.	Na <i>p</i> -xylene-2-sulphonate.
Solubility.	Not readily soluble in H ₂ O; soluble in hot alcohol, not readily in cold.	Soluble in H ₂ O; soluble in alcohol.	Not readily soluble in H ₂ O; a little soluble in hot alcohol; sparingly in cold.
Crystalline form.	Prisms or flat needles.	Well-defined rhombic plates.	Prisms or flat needles.
Optical properties.	Extinction straight; elongation positive.	} The same.	The same.
For cedar oil For C ₂ H ₄ Br ₂	$n_1 < N$. $n_1 < N < n_2$.		$n_1 > N$. $N < n_1 < n_2$.

The crystals of sodium sulphonate of *p*-xylene are distinguished from its isomers by its refractive indices. But the *o*- and *m*-compounds cannot be distinguished by this way, the only key in this case being their crystalline forms. The *m*-compound when slowly crystallises out from alcohol, forms well-defined rhombic plates, the two internal angles of which are about 80° and 100° respectively, while the *o*-compound crystallises in prisms or in flat needles. Consequently *o*-compound is detected by finding prismatic crystals whose smaller refractive index is lower than that of cedar oil.

It must be here added, however, that, as the crystalline forms of the salts of these sulphonic acids seem to have tendency to be easily disturbed by the presence of their isomers, we cannot expect the results of this method to be highly sensitive.

An Actual Example.

All the above mentioned methods were tested with various mixtures and proved to be applicable. An example of the analysis of commercial xylene shall be briefly described.

"Xylol" on market was distilled with Hempel's still-head, and two fractions, 135–8°C. and 140–2°C. were taken.

Detection of *m*- and *p*-xylenes. To 1 c.c. of the first fraction, 10 c.c. of the nitrating acid⁽¹⁾ (conc. H_2SO_4 1 : fuming HNO_3 2) were slowly added under water tap. The mixture was then heated in an oil bath at 110–120°C. for an hour, and the content was poured into water. The raw product was purified by washing with ether, and by recrystallising from a large amount of alcohol. Then the detection of isomeric xylenes in the sample was carried out in two ways.

By colour-reaction. When one portion of crystals thus obtained was tested in alcoholic solution with KOH, the intense green coloration instantly occurred. (Presence of *m*-xylene!) Next, the other portion was treated with hot acetone, when the greater part remained undissolved. (This shows that the sample was very rich in *m*-xylene.) The acetone solution gave the red coloration with KOH. (Presence of *p*-xylene!)

By microscopic method. Crystals, which remained undissolved in hot acetone, were examined under microscope; they had straight extinction and positive elongation, and their refractive indices stood in the following relation: $n_1 < \alpha\text{-bromonaphthalene} < n_2$. These crystals are nothing but trinitro-*m*-xylene. On the other hand, those separating out from acetone solution on cooling were found to be a mixture of two crystals, one of which was of positive elongation and the other negative, and the mixture contained the latter in far larger quantity. Those crystals with positive elongation proved to be trinitro-*m*-xylene from their refractive indices, and those of negative elongation were ascertained to be trinitro-*p*-xylene, for both of their refractive indices were greater than that of α -bromonaphthalene.

Detection of *o*-xylene. When 1 c.c. of the second fraction was shaken with equal volume of conc. H_2SO_4 at 80–90°C. for 30 minutes, nearly all the sample was absorbed in the acid. The sulphonic acids were converted into Ba salts in usual way, and from their aqueous solution two fractions of crystals were obtained. Dissolving each fraction in hot water, Ba was precipitated with a_2NCO_3 . The filtrate was evaporated to dryness, and the sodium sulphonates were extracted with hot alcohol.⁽²⁾ Crystals separating out from the somewhat concentrated alcoholic solution were not well-defined, and found in an aggregate state. Few prismatic crystals were found, but they proved to be the *p*-compound by their refractive indices. None of the crystals had properties of the *o*-compound, thus proving its absence.

To make sure, another c.c. of the second fraction was brominated with an excess of bromine in the presence of reduced iron. The product after

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- (1) An excess of nitrating acid must be added, otherwise, *p*-xylene forms only dinitro-derivatives which are readily soluble in ether.
 - (2) Sodium sulphonates were also prepared directly by dropping the mixture of the raw sulphonic acids with excess of conc. H_2SO_4 , in 4 times its volume of saturated NaCl solution.

washing with alkali and HCl successively, was several times recrystallised from chloroform, collecting every time crystals separating out first. Long white needles finally obtained melted at $252-3^{\circ}\text{C}.$, which is exactly the m. p. of the pure esotetrabromo-*p*-xylene.

Thus in the commercial xylene in question no appreciable quantity of *o*-xylene was detected.

Appendix.

As the above mentioned principle,⁽¹⁾ on which one of the technical methods of separating *p*-xylene from its isomers is based, seems to be very doubtful, I have re-examined the method.

Five hundred c.c. of the commercial xylene, same as that used in the above experiments, was shaken with equal volume of conc. H_2SO_4 for 30 min., and the unabsorbed portion, which was only few percent of the sample, was fractionated. The first drop distilled at $145^{\circ}\text{C}.$, and the thermometer rapidly rose to $160^{\circ}\text{C}.$, while the b. p. of *p*-xylene is $135-6^{\circ}\text{C}.$ Here, we can conclude that nearly all *p*-xylene was absorbed in sulphuric acid, consequently this technical method is not recommendable for that purpose.

Summary.

Methods to detect and identify the three isomeric xylenes in their mixture, especially in limited quantity, are given.

1. *m*-Xylene and *p*-xylene, even in minute quantity, can be successfully identified as their trinitro-derivatives, by their colour-reactions in alcoholic or acetone solution toward alkali, or by the optical properties of their crystals. These two methods leave little to be desired.

2. *o*-Xylene is identified microscopically as sodium sulphonate, but in case of a mixture very poor in *o*-xylene, we can not expect a result of high sensitivity by this method.

3. The technical method to separate *p*-xylene from its isomers, based on its insolubility in ordinary conc. sulphuric acid, is tested and shown to be of little value.

In conclusion, I must express my hearty thanks to Dr. I. Okada for his kind help in practical treatment of the microscope.

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(1) See p.196.

STUDIES ON THE BROMINATION OF TETRA-ETHYL DICARBOXY-GLUTACONATE AND REMARKS ON THE CONSTITUTION OF THE GLUTACONIC ACIDS.

By Yoshiyuki URUSHIBARA.

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In the last two years the author published some papers dealing with studies on the derivatives of glutaconic acid.⁽¹⁾ The first experiment was the bromination of tetraethyl dicarboxyglutaconate, the object of which was, in the first place, to obtain tetraethyl α, β -dibromodicarboxyglutarate; and this theme was given by Prof. K. Matsubara. Since the expected result was not obtained, it was given up without further investigations, and another compound with a similar constitution, diethyl dicyanoglutaconate, was taken as the substance to be subjected to the action of bromine. What the so-called diethyl dicyanoglutaconate is, and how it is acted on by bromine, were already described in details.⁽²⁾ In the meantime it seemed that some important results might be brought out by tracing the reaction between bromine and tetraethyl dicarboxyglutaconate. Experiments have been newly repeated, with the results described in the following pages.

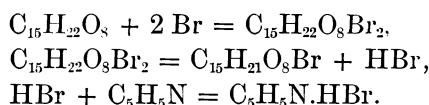
Action of Bromine on Tetraethyl Dicarboxyglutaconate. When bromine was added to the ester in the proportion of $2 \text{ Br} : \text{C}_{15}\text{H}_{22}\text{O}_8$, and the mixture was well stirred, the colour of bromine almost disappeared after a moment and hydrogen bromide was generated at the same time. The reaction mass was diluted with ether, shaken with aqueous alkali, washed with water, dried, and evaporated in vacuo. An oily substance remained; but hydrogen bromide was again generated.

The elimination of hydrogen bromide was completed through the following treatment. An ethereal solution of pyridine in an amount equimolecular to the ester was added to such of the reaction product of bromine and tetraethyl dicarboxyglutaconate. After standing for a night the ethereal solution was freed from pyridine hydrobromide by washing it with water, and further it was washed successively with dilute sulphuric acid, dilute alkali, and water. The solution was dehydrated and evaporated in vacuo over concentrated sulphuric acid, when a colourless oil was obtained which splitted off hydrogen bromide no more. 0.1858 And 0.1780 gr. of the substance gave respectively 0.0876 and 0.0843 gr. of AgBr. (Found: Br = 20.06; 20.15. $\text{C}_{15}\text{H}_{21}\text{O}_8\text{Br}$ requires Br = 19.54.%) In one experiment 29.8 gr. of the product was obtained from 24.2 gr. of $\text{C}_{15}\text{H}_{22}\text{O}_8$ and 11.7 gr. of bromine,

(1) This journal, 2 (1927), 26; 236; 278; 305; 3 (1928), 102.

(2) This journal, 2 (1927), 26.

the theoretical yield calculated from the following equations being 30 gr. It is shown by these numbers that the product was formed according to the following equations :



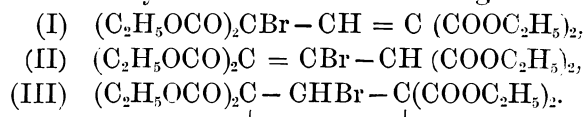
The reaction resulted as if a substitution took place, but really it consisted of two processes of addition of 2 Br and elimination of HBr, because the calculated amount of bromine was consumed at once, and the elimination of hydrogen bromide was not complete unless the product was treated with pyridine.

The intermediate product formed by addition of 2 Br to $\text{C}_{15}\text{H}_{22}\text{O}_8$, has, of course, the formula $\text{C}_{15}\text{H}_{22}\text{O}_8\text{Br}_2$ and the following constitution :



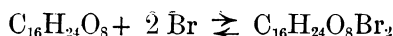
This addition product splits off a molecule of hydrogen bromide, and this dissociation is complete in the presence of pyridine which fixes the hydrogen bromide.

Hydrogen bromide may possibly be splitted in three ways, and the produced bromo-ester may have one of the following formulae :



It is impossible for such a three-carbon ring as shown by formula (III) to be formed by elimination of hydrogen bromide, and this formula is excluded, if the result of saponification of the bromo-ester is further taken into account. The bromo-ester possesses no acid hydrogen, for it does not dissolve in alkali, and formula (II) is also improbable. The following experiment settles the question, indicating that the bromo-ester is most reasonably represented by formula (I).

When bromine was added to tetraethyl α -methyldicarboxyglutaconate $(\text{C}_2\text{H}_5\text{OCO})_2\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{COOC}_2\text{H}_5)_2$, in which the acid hydrogen is replaced by a methyl group, a part of bromine combined with the ester after a short time, the colour fading to some extent, but never completely even if the bromine was used in an amount much smaller than two atoms to one molecule of the ester, while the elimination of hydrogen bromide was not detected. This observation ascertained the existence of equilibrium in the following reversible reaction :



In the ethereal solution this reaction is fixed. Thus, when the reaction mixture was dissolved in ether, shaken with an aqueous solution of sodium sulphite, washed with water, dried and evaporated in vacuo, the remaining

colourless oil soon spitted bromine and became red. The addition of bromine to tetraethyl dicarboxyglutaconate is nearly complete, causing the elimination of hydrogen bromide, and that to a limited extent, while the action of bromine on tetraethyl α -methyldicarboxyglutaconate can proceed only incompletely, the elimination of hydrogen bromide being impossible here. In both cases the saturated compounds formed by the addition of bromine is in equilibrium with unsaturated compounds, in the former case the unsaturated bromo-ester $C_{15}H_{21}O_8Br$ being produced by a secondary change of the saturated addition product, while in the latter a part of the original unsaturated ester being left intact. This difference must be attributed to the presence of the acid hydrogen in the one, and the absence in the other. In other words, when hydrogen bromide is splitted from the saturated dibromo-ester, the acid hydrogen takes part in the formation of hydrogen bromide. Therefore, the unsaturated bromo-ester $C_{15}H_{21}O_8Br$ misses the acid hydrogen and must be the compound represented by formula (I) which should be called tetraethyl α -bromodicarboxyglutaconate. The bromine atom remaining in the bromo-ester is situated in the γ -position of the original ester, tetraethyl dicarboxyglutaconate, but it may be designated as the α -substituent in conformity to the subsequent arrangement of the propylene nucleus, in which the single and the double bonds exchange their positions during the addition of bromine and elimination of hydrogen bromide.

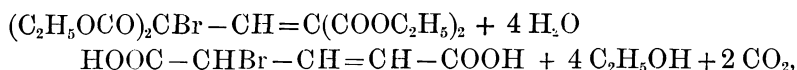
A substance with the same composition and constitution as the above bromo-ester has been already known and obtained by the interaction of bromine and the sodium or cupric derivative of tetraethyl dicarboxyglutaconate.⁽¹⁾ Recently F. Faltis and J. Pirsch⁽²⁾ obtained tetraethyl allene-tetracarboxylate by the action of silver oxide on this bromo-ester.

Hydrolysis of Tetraethyl α -Bromo-dicarboxyglutaconate. The bromo-ester, formed by the elimination of hydrogen bromide from the addition product of bromine to tetraethyl dicarboxyglutaconate, was hydrolysed by boiling with hydrochloric acid. The product was obtained in various grade of purities according to the conditions of saponification. It has been found that a large quantity of alcohol must be present in order to get the product in a state free from resinous coloured contamination, the presence of alcohol accelerating the reaction at the same time. The following proportion gave a good result. The mixture of the bromo-ester 25 gr., alcohol 70 gr., concentrated hydrochloric acid 100 gr., and water 30 gr, is boiled for 3 or 4 hours with a reflux condenser, and the solution is evaporated on the water bath. When the solution is evaporated to a small volume, a further amount of

(1) Guthzeit and Hartmann, *J. prakt. Chem.*, [2] 81 (1910), 350; F. Faltis and Carla Ruiz de Roxas, *Monatsh.*, 42 (1922), 459.

(2) *Ber.*, 60 (1927), 1621.

concentrated hydrochloric acid is added, the solution is evaporated to dryness, and the crystalline mass is dehydrated in a desiccator over concentrated sulphuric acid and soda-lime. In one experiment 24.6 gr. of the bromo-ester gave 9.3 gr. of the crude product in brownish crystals. If the saponification proceeded according to the equation :



the above quantity of the bromo-ester must yield 12.6 gr. of the product. This result suggested some unexpected change. In fact it was found that the saponification product was no longer a compound of bromine, but it contained chlorine. This crystalline compound was purified by repeated recrystallization from a little amount of water until it showed a nearly constant melting point 155° . In order to make the recrystallization most effective, it was necessary to remove entirely the mother liquor each time. The mother liquor was well drained off by sucking the crystals in a Gooch crucible with a filter paper fitted at the bottom, and pouring pure benzene on the crystals, the sucking being continued. After the last recrystallization the crystals were well dried over sulphuric acid. It is colourless, easily soluble in water, alcohol, acetic acid, acetone, and ether, but difficultly soluble in benzene and chloroform. It is readily oxidized by the alkaline permanganate solution and is found to be an unsaturated acid. 0.3498 Gr. of the substance gave 0.4662 gr. of CO_2 and 0.0954 gr. of H_2O ; 0.2134 gr. of the substance gave 0.2340 gr. of CO_2 and 0.0574 gr. of H_2O ; 0.2374 gr. of the substance gave 0.2042 gr. of AgCl . (Found: C=36.36, 36.31; H=3.05, 3.01; Cl=21.28. $\text{C}_5\text{H}_5\text{O}_4\text{Cl}$ requires C=36.47; H=3.06; Cl=21.56%.) It is doubtlessly a chloroglutaconic acid.

Hitherto only one chloroglutaconic acid has been known, and that is β -chloroglutaconic acid melting at 129° ⁽¹⁾. Now another chloroglutaconic acid melting at 155° has been obtained. These two kinds of acids are subjected to the similar treatment at the last process of preparation, that is, saponification with hydrochloric acid, and it is supposed that they are not geometrical isomers to each other. Hence the chloroglutaconic acid, the constitution of which is now under discussion, must be one of the following isomers :

(IV) α -chloroglutaconic acid, $\text{HOOC}-\text{CHCl}-\text{CH}=\text{CH}-\text{COOH}$;

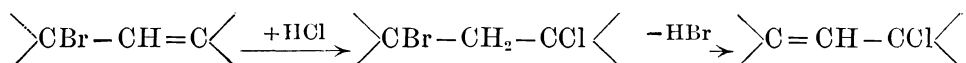
(V) γ -chloroglutaconic acid, $\text{HOOC}-\text{CH}_2-\text{CH}=\text{CCl}-\text{COOH}$.

Now it must be considered how the bromine atom in the bromo-ester $\text{C}_{15}\text{H}_{21}\text{O}_8\text{Br}$ is replaced by a chlorine atom during its saponification giving the chloroglutaconic acid. This is well understood if it is supposed that the

(1) Burton, Pechmann, *Ber.*, **20** (1907), 147; Inyold, Nickolis, *J. Chem. Soc.*, **121** (1922), 1638.

addition of hydrogen chloride and at the same time the elimination of hydrogen bromide take place. It is natural to consider that, if addition is easy to take place, then the inverse reaction may be also easily realised. Thus if the compound with bromine is less stable than that with chlorine in the saponifying medium where the concentration of hydrogen chloride is much greater than that of hydrogen bromide even after the replacement of the halogens has been finished, it is not surprising that the addition of hydrogen chloride and the elimination of hydrogen bromide take place simultaneously.

In whatever manner addition and elimination may take place, a compound of the type (V) can not be formed. Hence the chloroglutaconic acid in question must have formula (IV). Now, after the constitution of the saponification product has been determined in this way, the mechanism of the formation of the chloro-acid from the bromo-ester can be explained to some extent as follows :

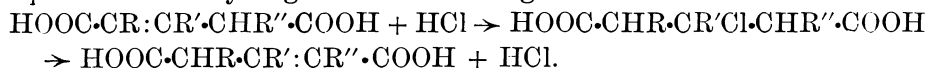


It is probable that hydrogen chloride adds in such a manner that enables the chlorine atom to take the position the most remote from the bromine atom. The above reaction may occur probably in every stage of the saponification.

The tetraethyl α -bromodicarboxyglutaconate prepared by Faltis' method was saponified by the same procedure, and the product was recrystallised from water several times. 0.2024 Gr. of the substance gave 0.2708 gr. of CO_2 and 0.0556 gr. of H_2O ; 0.2064 gr. of the substance gave 0.1724 gr. of AgCl . (Found: $\text{C}=36.50$; $\text{H}=3.07$; $\text{Cl}=20.66$. $\text{C}_5\text{H}_5\text{O}_4\text{Cl}$ requires $\text{C}=36.47$; $\text{H}=3.06$; $\text{Cl}=21.56\%$.) The quantity of the substance was too small to be purified to a constant melting point, but the substance melted at 154° , and the mixture of this specimen and the α -chloroglutaconic acid described in the preceding pages melted at 154° , which showed the identity of the two specimens.

By the studies described in this paper it has been found that in the derivative of glutaconic acid addition and simultaneous elimination can easily take place, and the most stable compound in the condition is obtained as the final product, without destroying the structure of the propylene chain. If the substance which adds to a glutaconic derivative is the same as that is eliminated from the intermediate saturated compound, this transformation will not be detected by analysis of the final product; but it is possible that the final product differs from the substance not yet subjected to this transformation; in other words, the movement of the double union is possible. For instance, if a glutaconic

derivative containing no halogen is hydrolysed with hydrochloric acid, hydrogen chloride may add to the unsaturated bond in such a manner that hydrogen will take the γ -position, chlorine the β -position, according to the usual rule of addition to an unsaturated acid, and then the chlorine may be splitted with α -hydrogen in the following manner :



This must be borne in mind when one carries out an experiment such as the saponification of the derivatives of glutaconic acid by means of hydrochloric acid. It is not meant that such a transformation can take place only in the derivatives of glutaconic acid, but that it is possible at least in this class of organic compounds. In one experiment of saponifying the bromo-ester, hydrochloric acid was replaced by sulphuric acid, and the product was examined. After removing the sulphuric acid by adding the calculated amount of barium carbonate, the solution was filtered from barium sulphate and evaporated on the water bath. On concentrating it the white fume of hydrogen bromide was evolved. The product, after recrystallisation from water, was found to contain nearly no halogen. Thus, in the saponification with sulphuric acid the reaction is also so complicated that the constitution of the product can be difficultly deduced from that of the starting substance.

This consideration may bring an important consequence upon the theory which has been held on the constitution of the glutacodic acids by certain investigators who have been working in this interesting field of organic chemistry.

Remarks on the Constitution of the Glutaconic Acids. In 1905 J. F. Thorpe⁽¹⁾ found that the α - and γ -positions in the glutaconic acids are the same, for instance, α , β -dimethylglutaconic acid $\text{HOOC}-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}-\text{COOH}$, and β , γ -dimethylglutaconic acid, $\text{HOOC}-\text{CH}_2-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{COOH}$, are identical. From this fact he gave the glutaconic acid and its derivatives the symmetrical formula, the so-called normal form, and the constitution of glutaconic acid was represented by the formula $\text{HOOC}-\underset{|}{\text{CH}}-\underset{|}{\text{CH}_2}-\underset{|}{\text{CH}}-\text{COOH}$. Since then he and his collaborators have been making many important investigations in this sphere, among which some indicated also the identity of the α - and γ -positions in the glutaconic acids.⁽²⁾ Feist⁽³⁾ rejected Thorpe's theory of the normal form, and has been supporting the ordinary formula until the present. Feist held the theory of oscillation in order to explain the existence of only one form of glutaconic acid and the

(1) *J. Chem. Soc.*, **87** (1905), 1669.

(2) *J. Chem. Soc.*, **89** (1906), 631; **99** (1911), 2187.

(3) *Ann.*, **345** (1906), 117; **370** (1909), 41; **428** (1922), 25.

identity of the α - and γ -positions of this acid, and he has been also making many important studies on the derivatives of this acid. Not only Feist, but also any other chemists, have not suspected the uncertainty involved in the experiments showing the identity of the α - and γ -positions of glutaconic acid, on which the standpoint of Thorpe's theory of the normal form was based. In all of the experiments which were taken as the proofs of the identity of the α - and γ -positions the substituted glutaconic acids were obtained by the saponification process with concentrated hydrochloric acid. Now, the present author has shown that the constitution (the position of the double union) of the product can not be deduced from that of the starting substance in a reaction such as the saponification of the glutaconic derivatives with hydrochloric acid. Thus the imperfection in Thorpe's conclusion is pointed out. If the experiments resulted as if the α - and γ -positions were the same, it must be rather concluded that the migration of the double union took place during the reaction. He recognised the migration of the double union when he dealt with the action of sodium ethylate on the derivatives of the glutaconic ester, and even a rule of migration of the double union was devised.⁽¹⁾ It is unnatural to assume the fixity of the double union in the saponification with hydrochloric acid and to conclude the identity of the α - and γ -positions.

A hypothesis as Thorpe's seems to be no longer necessary in the chemistry of the glutaconic acids, and, therefore, the present author will support the opinion held by Feist, but it seems that his theory of oscillation is also no longer indispensable, for it is now the fact of existence of only one form of glutaconic acid that this theory is to explain, and this fact can be easily understood if it is supposed that only one form is stable.

In the paper on the nitrile-esters of the dicarboxyglutaconic acid,⁽²⁾ the mechanism of the condensation of an ethoxymethylene compound $C_2H_5OCH=CXY$ with a sodio-methylene compound $CHNaX'Y'$ was explained on the assumption that the theory of the normal form can be applied to the derivatives of dicarboxyglutaconic acid. This explanation must be corrected according to the results of the recent investigations which showed that Thorpe's theory of the normal form had been based on somewhat uncertain evidences. In this paper it is stated only that the explanation must be corrected, and how the mechanism of the above condensation is correctly explained will be published in another paper, for it is necessary further to carry out such experiments as will throw light on the consideration of the reactions of this kind.

(1) *J. Chem. Soc.*, **101** (1912), 249.

(2) This journal, **2** (1927), 282.

Summary.

By the action of bromine, on tetraethyl dicarboxyglutaconate, tetraethyl α -bromodicarboxyglutaconate was obtained as the final product. When the tetraethyl α -bromodicarboxyglutaconate was saponified by means of hydrochloric acid, the product was α -chloroglutaconic acid. According to the result of this investigation, it was concluded that, when one carries out the saponification of a derivative of glutaconic acid, the constitution of the product cannot be deduced from the starting substance. Uncertainty in J. F. Thorpe's theory of the normal form was pointed out.

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ON ENANTIOTROPY AND MONOTROPY. II.

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The behaviours of dimorphism at constant pressure may be classified at least into three categories. The first is the case in which the transition occurs in the reversible manners or enantiotropy. The second is the case in which the transition is limited in one direction or monotropy. For the third we are able to consider a case in which the transition can not occur. In the preceeding paper⁽¹⁾ the typical thermodynamic relations for enantiotropy and monotropy were discussed in general and it was tried to supplement the studies in this field. In the present paper these relations will be discussed for the individual cases, especially in the case of monotropy.

The Thermodynamic Eormulae Concerning the Affinity of Transition.

As for the unit mass of the substance in one component, we have the following relations concerning the χ - and ζ - functions of Gibbs,

$$\left(\frac{\partial \chi}{\partial T}\right)_p = c_p,$$

$$\zeta = \chi - Ts = \chi + T \left(\frac{\partial \zeta}{\partial T}\right)_p,$$

$$\left(\frac{\partial \zeta}{\partial T}\right)_p = -s \quad \text{and} \quad \left(\frac{\partial \zeta}{\partial p}\right)_T = v,$$

where s , v , c_p are the entropy, the volume and the heat capacity at constant pressure respectively concerning unit mass, p and T being pressure and absolute temperature. As the difference of these quantities are always necessary, the difference of these functions as the result of a virtual transition at p and T , between the two modifications, $A \rightarrow B$ will be denoted by the corresponding large letters as follows, $Z = \zeta_B - \zeta_A$, $X = \chi_B - \chi_A$, $S = s_B - s_A$, $V = v_B - v_A$ and $C_p = c_{pB} - c_{pA}$, where X is the calorimetric heat of transition expressed after the manners of Berthelot and Thomsen and Z is often called the affinity of transition respectively concerning the transition $B \rightarrow A$.

It is evident that we have the following relations among these quantities,

(1) This journal, 3 (1928), 91.

$$\left(\frac{\partial X}{\partial T}\right)_p = C_p \quad (\text{Kirchhoff's law})$$

$$\text{or} \quad X = X_0 + \int_0^T C_p dT \quad \dots\dots\dots(1)$$

$$\text{and} \quad Z = X + T \left(\frac{\partial Z}{\partial T}\right)_p \quad (\text{Gibbs and Helmholtz's law})$$

$$\text{or} \quad d\left(\frac{Z}{T}\right)_p = -\frac{X}{T^2} \quad .$$

By the integration of the above equation at constant pressure, we have

$$\frac{Z}{T} = \frac{Z_{T_1}}{T_1} - \int_{T_1}^T \frac{X}{T^2} dT \quad . \quad \dots\dots\dots(2)$$

If we let the transition temperature be T_0 ($\neq 0$), we have

$$Z = -T \int_{T_0}^T \frac{X}{T^2} dT \quad . \quad \dots\dots\dots (2a)$$

If we assume after Nernst that

$$\lim_{T \rightarrow 0} \left(-\frac{\partial Z}{\partial T}\right)_p = \lim_{T \rightarrow 0} S = 0$$

$$\text{or} \quad S = \int_0^T \frac{C_p}{T} dT \quad ,$$

we have the following relations at constant pressure,

$$\begin{aligned} Z &= Z_0 - \int_0^T S dT && \left(\because \left(\frac{\partial Z}{\partial T}\right)_p = -S\right) \\ &= Z_0 - \int_0^T dT \int_0^T \frac{C_p}{T} dT \\ &= Z_0 - T \int_0^T \frac{dT}{T^2} \int_0^T C_p dT \\ &= X_0 - T \int_0^T \frac{X - X_0}{T^2} dT \quad . \quad \dots\dots\dots(3) \end{aligned}$$

$$\text{And we have} \quad \left(\frac{\partial Z}{\partial p}\right)_T = V \quad .$$

By the integration at constant temperature, we have

$$Z = Z_{p_1} + \int_{p_1}^p V dp \quad . \quad \dots\dots\dots (4)$$

The formulae (2) and (2a) show that we can estimate the affinity of transition within the range of temperature for which the specific heats of the

two modifications are known, the affinity and the heat of transition being observed at any temperature within it. On the other hand, the formula (3) shows that we are able to estimate the affinity of transition from absolute zero to any temperature if we know the specific heats for the corresponding range of temperature and the heat of transition at any temperature within it.

Evaluation of the Affinity of Transition. From the thermodynamic standpoint, the most thoroughly studied examples can be found in the dimorphism of sulphur⁽¹⁾ and tin.⁽²⁾ In the former case, the affinity of transition was estimated on the basis of the Nernst's theorem or by the formula (3). In the latter case, it was evaluated by the formula (2a) or on the basis of the second law of thermodynamics, from the transition temperature down to absolute zero. As the result of which the Nernst's theorem was verified. These are the typical cases of enantiotropy and the Z-curves (or affinity curves) are as in the Fig. 4 in the preceding paper. In these cases the transition point is fairly clear and the affinity of transition may also be estimated directly by the measurement of solubility⁽³⁾ or e.m.f.,⁽⁴⁾ although the range of temperature is narrowly limited. Therefore, it is able to estimate the affinity of transition within a wide range of temperature on the mere basis of the second law of thermodynamics.

In the case of diamond and graphite, however, so far as the experiments are concerned, it is almost impossible to measure the affinity of transition directly. This system was first studied by Roozeboom⁽⁵⁾ from the standpoint of phase theory and was ascribed to the category of pseudomonotropy, although its theoretical ground is not very accurate. It seems interesting to treat it on the basis of the Nernst's theorem, for by the sole means of which we are able to evaluate the affinity of transition quantitatively. Roth⁽⁶⁾ observed the heat of transition as follows,

$$\text{Diamond} = \text{Graphite} + 156 \text{ cal./gr. atom. (at } 290^\circ\text{K.)}$$

As for the specific heats of diamond and graphite, the Nernst's⁽⁷⁾ data have been taken for the lower temperatures and the Magnus⁽⁸⁾ data for the higher temperatures from 300°K. to 1100°K. The values of the heat of transition have been calculated by means of the formula (1) from 0°K to 1100°K. Next, the values of the affinity of transition have been calculated by the formula (3). In the above calculations, the Debye's T^3 law has been applied for the

(1) W. Nernst, "Grundlagen des neuen Wärmesatzes" (1918), p. 87.

(2) J. N. Brønsted, *Z. physik. Chem.*, **83** (1914), 479. cf. F. Lange, *ibid.*, **110** (1924) 343.

(3) J. N. Brønsted, *ibid.*, **56** (1906), 645.

(4) E. Cohen, *ibid.*, **30** (1899), 614.

(5) H. W. B. Roozeboom, "Die heterogenen Gleichgewichte" (1901), p. 179.

(6) W. A. Roth and H. Wallasch, *Z. Elektrochem.*, **21** (1915), 1.

(7) W. Nernst, *Ann. Physik*, **36** (1911), 396.

(8) A. Magnus and A. Hodler, *ibid.*, **80** (1926), 808; A. Magnus, *ibid.*, **70** (1923), 303.

calculation of the specific heats at the lowest temperatures, and the method of graphical integration has been used for the higher temperature. The results obtained are shown in the following table and in Fig. 1. In which $X = \chi_{\text{diamond}} - \chi_{\text{graphite}}$ and $Z = \zeta_{\text{diamond}} - \zeta_{\text{graphite}}$. Therefore Z may be understood as the affinity of transition and X the heat of transition from diamond to graphite.

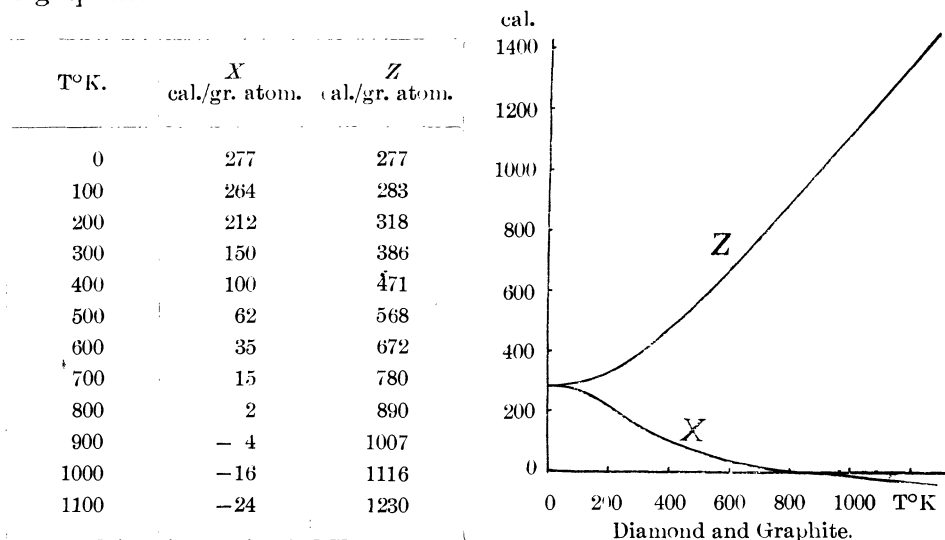


Fig. 1

These values will also be reproduced within the limits of a few percent if we apply the Debye's functions for the specific heats,

$$c_p \text{ diamond} = D\left(\frac{1900}{T}\right) + 1.9 \times 10^{-6} T^{\frac{3}{2}};$$

$$c_p \text{ graphite} = \frac{1}{3} \left[2D\left(\frac{2280}{T}\right) + D\left(\frac{760}{T}\right) \right] + 4.0 \times 10^{-6} T^{\frac{3}{2}}$$

where

$$D\left(\frac{\theta}{T}\right) = 3Nk \left[\frac{12}{x^3} \int_0^{\infty} \frac{\xi d\xi}{e^{\xi} - 1} - \frac{3x}{e^x - 1} \right],$$

$$x = \frac{\theta}{T} = \frac{h\nu_{\text{max.}}}{kT} \quad \text{and} \quad \xi = \frac{h\nu}{kT}.$$

The nature of the Z -curve in Fig. 1 shows that graphite is more stable than diamond in the range from 0°K. to 1100°K. And it is a well known fact that diamond is unstable at the higher temperatures above it. Out of these considerations, we are able to confirm that the dimorphism of diamond and graphite is truly monotropic, instead of being pseudomonotropic.

(1) P. Debye, *Ann. Physik*, 39 (1912), 789.

(2) Strictly speaking, it is necessary to add the condition, "under the atmospheric pressure," however, it will be omitted when clear.

Furthermore, the X -curve in Fig. 1 shows that the heat of transition changes its sign at ca. 850°K . Above this temperature diamond seems to transform into graphite with the absorption of heat. It had been considered by some authors as one of the characteristic properties of monotropy that the unstable modification changes into the stable with the evolution of heat.⁽¹⁾ However, it may be mentioned here that even if there exist always stable and unstable modifications, the transition will not always occur with the evolution of heat, as is clear by the behaviours of Z - and X -curves in Fig. 1.

An analogical case will be found in the dimorphism of white and red phosphorus. As red phosphorus is nonvolatile and practically insoluble in many solvents below the ordinary temperature, it is also difficult to estimate the affinity of transition between them directly. Similar estimation on the basis of the Nernst's theorem have been carried out. As for the heat of transition, the Giran's⁽²⁾ data have been taken,

Red phosphorus = White phosphorus + 3.70 Kcal./gr. atom (290°K .)

With regard to the specific heats, the data of Wigand⁽³⁾ and Ewald⁽⁴⁾ have been taken. The data of the specific heats are not very accurate in this case. However, the heat of transition is so large that the accuracy of the specific heats has no much influence upon the evaluation of the affinity of transition and the heat of transition. The results are shown in the following table and in Fig. 2, in which Z and X are the affinity and the heat of transition from white to red phosphorus respectively.⁽⁵⁾

T $^{\circ}\text{K}$.	X Kcal./gr. atom	Z Kcal./gr. atom.
0	3.67	3.67
50	3.69	3.66
100	3.75	3.61
150	3.77	3.54
200	3.76	3.47
250	3.73	3.39
300	3.69	3.33

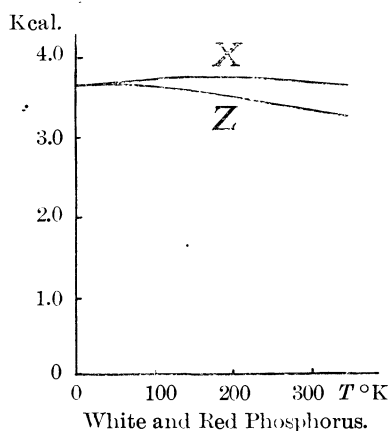


Fig. 2.

- (1) H. W. B. Roozeboom, loc. cit.; cf. the quotation of O. Lehmann in the preceeding paper.
- (2) Giran, *Ann. chim. phys.*, **30** (1903), 203.
- (3) A. Wigand, *Ann. Physik*, **22** (1907), 64.
- (4) R. Ewald, *ibid.*, **44** (1914), 1213.
- (5) As white phosphorus has a transition point at ca. -78°C ., the white phosphorus above given is the form with the melting point at 44°C . cf. Bridgman, *J. Am. Chem. Soc.*, **36** (1914), 1244.

The affinity curve in Fig. 2 shows that red phosphorus is more stable than white phosphorus from absolute zero to the melting point of the white phosphorus. It is, therefore, truly monotropic, although it was supposed to be pseudomonotropic by Findlay.⁽¹⁾

In certain cases of dimorphism, however, one modification exists in a very narrow range of temperature. So that the above given method to determine the relation of mutual stability on the rigorous bases of the second law and the Nernst's theorem will fail, for the specific heats will not completely be measured. If the melting points and the latent heats of fusion of the both forms are known, however, we are able to derive an approximation formula for the estimation of the affinity of transition. After Nernst we may put, for the first approximation, that

$$X = X_0 + \beta T^2 \quad \text{and} \quad Z = X_0 - \beta T^2.$$

If we apply these formulae to the relations between the liquid phase and the modification A , we have

$$X_A = \chi_l - \chi_A = X_{A0} + \beta_A T^2, \quad \dots\dots\dots(5)$$

$$\text{and} \quad Z_A = \zeta_l - \zeta_A = X_{A0} - \beta_A T^2, \quad \dots\dots\dots(6)$$

where χ_l and ζ_l are the specific values of χ - and ζ -functions of Gibbs concerning the liquid phase respectively.

At the melting point T_A , we have $Z_A = 0$. Therefore, from (6), we have

$$\beta_A = \frac{X_{A0}}{T_A^2}.$$

Putting it in (5), we have

$$X_{A0} = \frac{1}{2} \lambda_A \quad \text{and} \quad \beta_A = \frac{1}{2} \frac{\lambda_A}{T_A^2},$$

where λ_A is the heat of fusion at the melting point T_A . Accordingly we have

$$Z_A = \frac{1}{2} \lambda_A - \frac{1}{2} \frac{\lambda_A}{T_A^2} T^2.$$

Similarly

$$Z_B = \frac{1}{2} \lambda_B - \frac{1}{2} \frac{\lambda_B}{T_B^2} T^2.$$

where $Z_B = \zeta_l - \zeta_B$, λ_B being the latent heat of fusion at the melting point T_B of the modification B .

Henceforth we have,

$$\begin{aligned} Z &= \zeta_B - \zeta_A = Z_A - Z_B = X_0 - \beta T^2 \\ &= \frac{1}{2} (\lambda_A - \lambda_B) - \frac{1}{2} \left(\frac{\lambda_A}{T_A^2} - \frac{\lambda_B}{T_B^2} \right) T^2 \dots\dots\dots(7) \end{aligned}$$

(1) A. Findlay, "The Phase Rule" (1920); p. 48.

or

$$X_0 = \frac{1}{2}(\lambda_A - \lambda_B) \quad \text{and} \quad \beta = \frac{1}{2} \left(\frac{\lambda_A}{T_A^2} - \frac{\lambda_B}{T_B^2} \right).$$

Putting $Z=0$, we have the transition temperature T_0 between the two modifications A and B ,

$$T_0 = \left(\frac{\lambda_A - \lambda_B}{\frac{\lambda_A}{T_A^2} - \frac{\lambda_B}{T_B^2}} \right)^{\frac{1}{2}} \quad \dots \dots \dots (8)$$

With regard to the dimorphism of sulphur,⁽¹⁾

$$T_A = 388^\circ\text{K.}, \quad \lambda_A = 15.7 \text{ cal./gr.} \quad (\text{rhombic sulphur})$$

and $T_B = 392^\circ\text{K.}, \quad \lambda_B = 12.5 \text{ cal./gr.} \quad (\text{monoclinic sulphur})$

Putting these values in the formulae (7) and (8), we have

$$Z = 1.60 - 1.16 \times 10^{-6} T^2 \text{ cal./gr.},$$

and $T_0 = 372^\circ\text{K.} \quad (\text{obs. } 368^\circ\text{K.})^{(2)}$

As for ethyl ether, we have following data,

$$T_A = 157^\circ\text{K.}, \quad \lambda_A = 27.0 \text{ cal./gr.},^{(3)}$$

and $T_B = 150^\circ\text{K.}, \quad \lambda_B = 18.9 \text{ cal./gr.}^{(4)}$

Accordingly we have,

$$Z = 4.05 - 2.53 \times 10^{-4} T^2 \text{ cal./gr.}$$

and $T_0 = 177^\circ\text{K.} \quad (\text{above the melting points of the two modifications}).$

The values obtained by the above formula are shown in Fig. 3, which shows that the modification with the melting point at 150°K. is more stable than the modification with the melting point at 157°K. in the range from 0°K. to 177°K. We may therefore consider that this dimorphism of ethyl ether is monotropic.

Although it is difficult to expect much accuracy from it, we are able to find that similar monotropic relations also hold for the dimorphisms in iodine monochloride,⁽⁵⁾ benzophenone, bromonitrobenzene, phthalide, acetamide, monochloroacetic acid, nitro-*p*-toluide and erythrite.⁽⁶⁾ The values of X_0 and β are shown in the following table together with the data necessary for their evaluations.

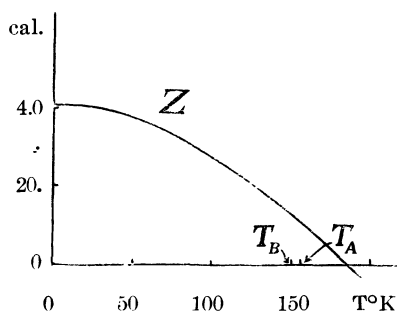


Fig. 3

(1) G. Tammann, "Kristallisieren und Schmelzen" (1903), p. 273.

(2) The results are in good coincidence with the estimation of Nernst, who obtained β by the data of specific heats.

(3) Beckmann and Waentig, *Z. anorg. allgem. Chem.*, **67** (1910), 17.

(4) S. Mitsukuri, this journal, **1** (1926), 30.

(5) Stortenbeker, *Z. physik. Chem.*, **10** (1892), 187.

(6) A. H. R. Müller, *ibid.*, **86** (1913), 237.

Substance	T_A °K	λ_A cal./gr.	T_B K°	λ_B cal./gr.	X_0 cal./gr.	$\beta \times 10^5$
Iodine monochloride	300	16.4	287	14.0	1.20	0.60
Benzophenone	321	23.4	298	17.9	2.75	1.25
Bromonitrobenzene	332	29.3	308	21.0	4.15	2.75
Phthalide	346	39.4	333	20.0	9.70	7.40
Acetamide	355	66.1	344	57.0	4.55	2.05
Mono-chloroacetic acid	334	40.7	329	35.2	2.75	1.85
Nitro- <i>p</i> -toluene	366	30.0	365	26.7	1.65	1.15
Erythrite	390	43.7	377	38.0	2.85	1.00

In short, if the two modifications have a sharp transition point, it may be easy to ascribe it to enantiotropy. However, even if we observe the transition only in one direction within a limited range of temperature, it is rather difficult to ascribe it to monotropy. For the phase changes between the two modifications are often disturbed by the effects of retardation, and in certain occasions, the enantiotropic dimorphism may manifest itself like monotropic. It may form one of the cases of pseudomonotropy. Accordingly, if we would to ascribe any dimorphism to monotropy, the affinity of transition should be estimated over a wide range of temperature. Although we know of many cases supposed to be monotropic, the affinities of transition connected to them have not fully been testified so far. In the above discussions, it has been tried to estimate the affinity of transition for such cases.

Effects of Pressure on the Affinity of Transition. In the preceeding paragraphs, the effects of pressure on the mutual stability of dimorphism have not been estimated. The affinity of transition under high pressure will be estimated by the formula (4), by which it is meant that we are able to estimate the affinity of transition at any pressure p if we know the affinity of transition at certain pressure p_1 and the specific volumes of the two modifications between p_1 and p . Therefore, it may be able to determine whether or not it is enantiotropic under high pressure, if we know the affinity of transition at one atmospheric pressure and the necessary data of the specific volumes. As for the case of diamond and graphite, we have

$$\begin{aligned}
 V &= v_{\text{diamond}} - v_{\text{graphite}} \\
 &= 12(1/3.5 - 1/2.3) = -1.79 \text{ cm.}^3/\text{gr. atom. (1 atm.)}
 \end{aligned}$$

For the first approximation, we may put

$$\begin{aligned}
 \int_1^p V dp &= p V \\
 &= -1.79 p \text{ atm. cm.}^3/\text{gr. atom.} = -0.0433 p \text{ cal./gr. atom.}
 \end{aligned}$$

As we have gained (page 212) that $Z_{300^\circ\text{K.}} = 386 \text{ cal./gr. atom.}$, and $\int_1^{10000} V dp$

$= -433$ cal./gr. atom., we may consider that there will be a transition point at 300°K , under the pressure of ca. 10^4 atms. and that the case of diamond and graphite is probably enantiotropic under the pressure of ca. 10^4 atms. Whereas in the case of white and red phosphorus, the affinity of transition is enormous and $V = +3.17$ cm³/gr. atom (1 atm.). Therefore it will remain monotropic even under the fairly high pressure.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima whose counsels have been constantly at his disposal.

Summary

1. The affinity of transition and the heat of transition from diamond to graphite and from white phosphorus to red phosphorus have been evaluated on the basis of the Nernst's theorem and it has been made clear that they are monotropic under the atmospheric pressure. The former case will probably be enantiotropic under high pressure, whereas the latter case will remain monotropic even under high pressure.

2. An approximation formula for the estimation of the affinity of transition has been derived and by means of which the dimorphisms in ethyl ether, iodine monochloride, benzophenone, phthalide, bromonitrobenzene, acetamide, monochloroacetic acid, nitro-*p*-toluene and erythrite have been estimated to be monotropic.

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**ETHYL 1:2:3:6-TETRACARBETHOXY-5-METHOXY- $\Delta^{2:5}$ -
CYCLOHEXADIEN-1-ACETATE, A DERIVATIVE
OF TRIETHYL ACONITATE.**

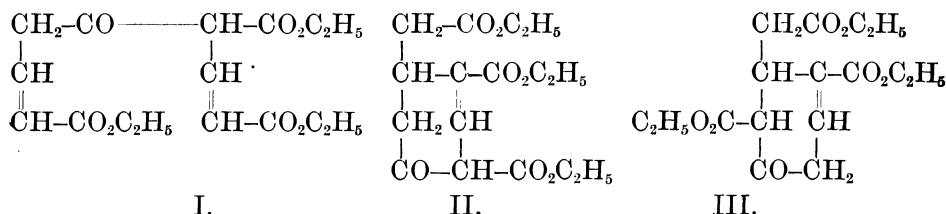
By Yoshiyuki URUSHIBARÄ.

Received July 24, 1928. Published September 28, 1928.

For a certain purpose the author tried the methylation of triethyl aconitate. A mixture of this ester and sodium ethylate in molecular proportion was heated on the water bath with an excess of methyl iodide in absolute alcoholic solution. As the reacting mixture was not brought to complete neutralisation in the course of one hour, it was heated at 115–120° under pressure. By this treatment the dark colour of the mixture faded to light brown. After concentrating the alcoholic solution, it was added to water

and extracted with ether. The ethereal extract gave a very viscous, fluorescent, slightly yellowish oil, which distilled at 225–230° under the pressure of about 1 mm.. It was purified by redistillation. 0.2220 Gr. of the substance gave 0.4632 gr. of CO₂ and 0.1340 gr. of H₂O; 0.2929 gr. of the substance gave 0.6110 gr. of CO₂ and 0.1747 gr. of H₂O. (Found: C=56.92, 56.91; H=6.75, 6.67%.) The numbers 491, 475, and 475 (mean 480) were obtained in the ebullioscopic determination of the molecular weight using acetone as the solvent. The analytical result corresponds to the formula C₂₃H₃₂O₁₁ which requires C=56.99, H=6.67%, and molecular weight=484. The obtained substance was not the methyl derivative of triethyl aconitate C₁₃H₂₀O₆ which requires C=57.31; and H=7.41%. If two molecules of triethyl aconitate C₁₂H₁₈O₆ split out one molecule of alcohol, and one hydrogen atom be substituted with a methyl group, that is, 2C₁₂H₁₈O₆ – C₂H₆O + CH₂, the formula C₂₃H₃₂O₁₁ is obtained. Before entering the problem of the constitution of this substance, some statements on the condensation of diethyl glutaconate are indispensable.

E. E. Blaise⁽¹⁾ obtained a condensation product of diethyl glutaconate when he tried the methylation of this ester at a high temperature. He showed that this substance was formed by the action of sodium ethylate on the glutaconic ester, two molecules of the latter splitting one molecule of alcohol. He gave it formula I. To the same substance H. v. Pechmann, W. Bauer, and J. Obermiller⁽²⁾ gave formula II, while R. Curtis and J. Kenner⁽³⁾ accepted formula III.



The last formula seems to be the most reasonable, and according to Curtis and Kenner this compound (in its enolic form) is called ethyl 2:6-dicarb-ethoxy- $\Delta^{2,5}$ -cyclohexadien-5-ol-1-acetate. Blaise⁽⁴⁾ tried the methylation of this compound and obtained a methyl derivative although not in a pure state.

In the present case, it is most probable that triethyl aconitate first gives the condensation product IV,⁽⁵⁾ or, strictly speaking, its sodium derivative,

(1) *Bull. soc. chim.*, [3] 29 (1903), 1028.

(2) *Ber.*, 37 (1904), 2113.

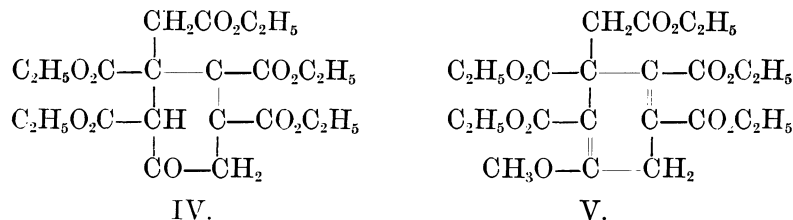
(3) *J. Chem. Soc.*, 105 (1914), 282.

(4) *Loc. cit.*

(5) The mechanism of formation, cf. *Ber.*, 37 (1904), 2114.

and this is further methylated by the action of methyl iodide. Thus the compound with the formula $C_{23}H_{32}O_{11}$ is obtained. This substance does not dissolve in aqueous alkali, and gives no colouration on adding ferric chloride. It does not condense with phenylhydrazine by the same treatment as that which enabled Curtis and Kenner to obtain the phenylhydrazide of the compound represented by the formula III.⁽¹⁾

This fact suggests that the methyl group in the compound $C_{23}H_{32}O_{11}$ is combined as a methoxy group, and that the intermediate product IV reacts in the enolic form, giving finally the methylated product V.



Thus the constitution of the substance formed in the methylating reaction of triethyl aconitate at 115–120° is represented by the formula V, and may be called ethyl 1:2:3:6-tetracarbethoxy-5-methoxy- $\Delta^{2,5}$ -cyclohexadien-1-acetate.

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(1) Blaise states that he obtained phenylhydrazone of the substance formed by methylating the condensation product of diethyl glutaconate, but the present author does not believe the correctness of Blaise's view.

SUPPLEMENTARY STUDIES ON THE NITRILE-ESTERS OF
THE DICARBOXYGLUTACONIC ACID.⁽²⁾

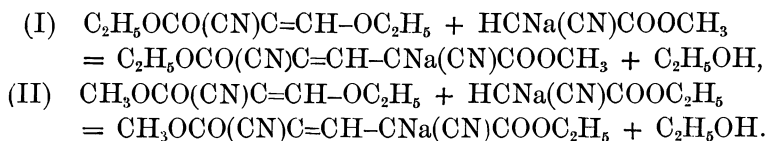
By Yoshiyuki URUSHIBARA.

Received August 21, 1928. Published September 28, 1928.

Methyl Ethyl Dicyanoglutaconate.⁽³⁾ The sodium derivative of this mixed ester is to be obtained (I) by the condensation of ethyl ethoxy-methylene-cyanoacetate with methyl sodio-cyanoacetate, and (II) by the condensation of methyl ethoxy-methylene-cyanoacetate with ethyl sodio-cyanoacetate, according to the following equations:

(2) For the completion of the studies published in this journal, **2** (1927), 278.

(3) Diethyl and dimethyl compounds: this journal, **2** (1927), 26, 236, 283.



As is evident from the above equations, the products of the two reactions are apparently different in the positions of the sodium atom and the double union, but it can be expected that they will prove to be identical as in the other cases.

Each of the condensations (I) and (II) was carried out (a) in ethyl alcohol and (b) in methyl alcohol. The experimental procedure common to these four kinds of reactions was as follows: Metallic sodium (1 mol) was dissolved in alcohol, the cyanoacetic ester (1 mol) was added, and then the ethoxy-methylene-compound (1 mol) was introduced. The sodium derivative of the dicyanoglutaconic ester separated out in yellow crystals. It was recrystallised from water, when it became nearly colourless, and then was transformed into the semihydrate by the action of dilute hydrochloric acid, which was examined.

(Ia) The product was wholly *diethyl* dicyanoglutaconate semihydrate ($\text{C}_{11}\text{H}_{12}\text{O}_4\text{N}_2$) $\cdot$ $\frac{1}{2}$ H_2O with the melting point 184° .

(Ib) The product was found to be *methyl ethyl* dicyanoglutaconate semihydrate with the melting point 197° (corr.). 0.2232 Gr. of the substance gave 23.6 c.c. of nitrogen at 18.5° , 761.0 mm. (Found: N=12.14. ($\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_2$) $\cdot$ $\frac{1}{2}$ H_2O requires N=12.12%.)

(IIa) The product was the same as that of (Ib). 0.1754 Gr. of the substance gave 18.45 c.c. of nitrogen at 18° , 762.4 mm. (Found: N=12.13%.) The specimens of (Ib) and (IIa) and their mixture melted at the same point 197° .

(IIb) The product was wholly *dimethyl* dicyanoglutaconate semihydrate ($\text{C}_9\text{H}_8\text{O}_4\text{N}_2$) $\cdot$ $\frac{1}{2}$ H_2O with the melting point 224° .

Thus it has been found that the cyanoacetic ester exchanges its alcohol group when it is converted into the sodium derivative by the action of sodium alcoholate. The exchange of the alcohol group can not take place in the products of the above condensations, for, when dimethyl sodio-dicyanoglutaconate was dissolved in ethyl alcohol, and the solution was boiled for one hour, none of the methyl groups was replaced by an ethyl group.

Mixed Esters of Dicarboxyglutaconic Acid. The condensation of dimethyl malonate with diethyl ethoxy-methylene-malonate was carried out (a) in ethyl alcohol, and (b) in methyl alcohol. The formed sodium compounds were recrystallised from ethyl alcohol. The free esters were obtained by the action of dilute hydrochloric acid in the aqueous solutions. In analysis, the product of (a) gave approximately the numbers calculated for *methyl triethyl*

ester. (Found: C=53.67; H=6.51. $C_{14}H_{20}O_8$ requires C=53.14; H=6.38%.) The product of (b) gave nearly the numbers for *dimethyl diethyl ester*. (Found: C=51.16; H=5.91. $C_{13}H_{18}O_8$ requires C=51.64; H=6.01%.)

The malonic ester also exchanges one of its alcohol groups when it is converted into the sodium derivative by the action of sodium alcoholate. Thus, after dimethyl malonate was acted by sodium ethylate, it reacted as if it were methyl ethyl malonate.

The Constitutions of the Sodium Derivatives of the Nitrile-esters of Dicarboxyglutaconic Acid. Those having symmetrical arrangement of cyano- and carbethoxy-groups afford no problem concerning their constitutions, and they are:

- (I) $(C_2H_5OCO)_2C=CH-CNa(COOC_2H_5)_2$;
- (II) $C_2H_5OCO(CN)C=CH-CNa(CN)COOC_2H_5$;
- (III) $(CN)_2C=CH-CNa(CN)_2$.

The free ester, tetraethyl dicarboxyglutaconate, obtained by acidifying the aqueous solution of the sodium compound (I), gives blue colour on adding ferric chloride to its alcoholic solution, showing that it is, at least partly, in the enolic form.⁽¹⁾ Tetracyanopropylene $(CN)_2C=CH-CH(CN)_2$ obtainable in solutions from the sodium derivative (III) was found to give no colouration with ferric chloride. Since the free nitrile-ester corresponding to the sodium compound (II) is not obtainable,⁽²⁾ another compound is to be examined instead of it, in order to know whether it would give colouration with ferric chloride or not, if it should exist. Fortunately, diethyl α , γ -dicyano- β -methyl-glutaconate $C_2H_5OCO(CN)C=C(CH_3)-CH(CN)COOC_2H_5$ is obtainable from its sodium derivative.⁽³⁾ This substance was found to give no colouration with ferric chloride. Thus the compounds in which the carbon atom retaining the sodium atom possesses two carbethoxy-groups are characterised with the colouration. The ferric chloride test carried out directly on the sodium compounds (I), (II), and (III) in their alcoholic solutions led to the same conclusion.

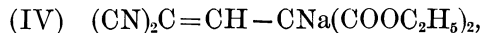
Now, the constitutions of the sodium derivatives of the other nitrile-esters of dicarboxyglutaconic acid can be determined by the reaction with ferric chloride. By the previous investigation it was found that the condensation of diethyl ethoxy-methylene-malonate with sodio-malonitrile, and the condensation of ethoxy-methylene-malonitrile with diethyl sodio-malonate give the same sodium compound, from which the same diethyl dicarbamyl-propylene-dicarboxylate is obtained. Then it was shown that the sodium

(1) H. Stobbe u. F. Wildensee, *J. prakt. Chem.*, **115** (1927), 163.

(2) This journal, **2** (1927), 26.

(3) This journal, **3** (1928), 102.

compound formed in the two reactions must have one of the two following formulae.

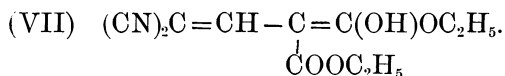
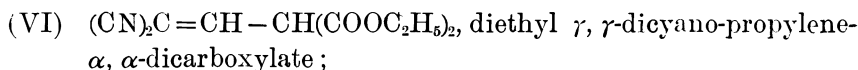


but it was not decided which is the constitution of the substance. This sodium compound gives an oily deposit on acidifying its aqueous solution, which dissolves again in the mother liquor when it is left there for a while and is transformed into the crystals of diethyl dicarbamyl-propylene-dicarboxylate.

The oily substance deposited from the aqueous solution of the sodium compound was quickly extracted with ether and the ethereal solution was washed with water, dehydrated with calcium chloride, and evaporated in vacuo. The oily residue was dissolved in alcohol. This alcoholic solution gave bluish violet colour on adding ferric chloride, showing that the oily substance is in the enolic form. The sodium compound itself gave violet colour on adding ferric chloride to its alcoholic solution.

The oily substance from both the sodium derivative obtained by the condensation of diethyl ethoxy-methylene-malonate with sodio-malonitrile, and that obtained by the condensation of ethoxy-methylene-malonitrile with diethyl sodio-malonate, gave the same colouration with ferric chloride.

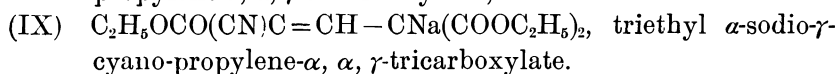
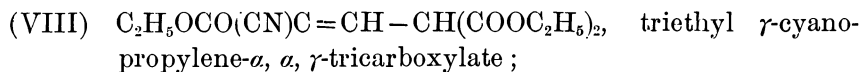
It is evident that the oily substance is the free nitrile-ester corresponding to the sodium compound. If it gives a colouration with ferric chloride, its constitution must be represented by formula (VI), or, in the enolic form, by formula (VII), and its sodium derivative by formula (IV).



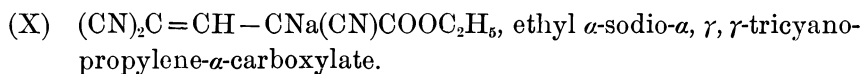
The alcoholic solution of this enolic cyano-ester gave a colourless crystalline deposit on standing for a while. After this transformation it gave no colouration with ferric chloride. It was also experienced that the colour given by a fresh alcoholic solution on adding ferric chloride faded gradually. The crystals were collected, washed with alcohol, and dried in a desiccator. This crystalline substance melts at 212°. 0.1149 Gr. of the substance gave 0.2185 gr. of CO₂ and 0.0580 gr. of H₂O; 0.0608 gr. of the substance gave 5.85 c.c. of nitrogen at 18°, 758.5 mm. (Found: C=51.88; H=5.65; N=11.03. C₁₁H₁₂O₄N₂·H₂O requires C=51.95; H=5.55; N=11.03%.) The analytical result corresponds to the monohydrate of diethyl dicyano-propylene-dicarboxylate, and one of the cyano-groups is hydrated into a carbamyl-group.

Of course, it has the configuration of diethyl γ -cyano- γ -carbamypropylene- α , α -dicarboxylate, $\text{H}_2\text{NCO}(\text{CN})\text{C}=\text{CH}-\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$, and, therefore, the dihydrate⁽¹⁾ is diethyl γ , γ -dicarbamypropylene- α , α -dicarboxylate, $(\text{H}_2\text{NCO})_2\text{C}=\text{CH}-\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$. While the enolic nitrile-ester is gradually transformed into the ketonic form, it is at the same time changed into the dicarbamy compound in the aqueous solution, and into the monocyanomonocarbamy compound in the alcoholic solution.

Triethyl cyano-propylene-tricarboxylate (cyano-carboxyglutaconate) gives violet colour on adding ferric chloride to its alcoholic solution. Hence formula (VIII) must be assigned to this cyano-ester, and formula (IX) to its sodium derivative.



The examples already described suggest that the sodium atom is generally retained by the carbon atom with the most carbethoxy-groups. For this reason the constitution of the ethyl sodio-tricyano-propylene-carboxylate may be represented by formula (X).



The compounds obtained by the action of a dilute acid on the sodium compounds, the free nitrile-esters or the various hydrates,⁽²⁾ may be considered to have the same configurations as the corresponding sodium derivatives. There has been nearly nothing to suggest the configuration of methyl ethyl sodio-dicyanoglutaconate.

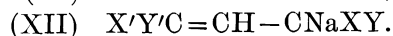
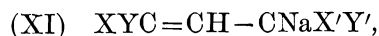
The Mechanism of the Condensation of an Ethoxy-methylene Compound $\text{C}_2\text{H}_5\text{OCH}=\text{CXY}$ with a Methylene Compound $\text{CH}_2\text{X}'\text{Y}'$ in the Presence of Sodium Alcoholate. In the previous paper on the nitrile-esters of the dicarboxyglutaconic acid, the mechanism of the condensation of an ethoxy-methylene compound with a sodio-methylene compound (or methylene compound in the presence of sodium alcoholate) was explained on the assumption that Thorpe's theory of the normal form can be applied to the derivatives of dicarboxyglutaconic acid. But this theory was found to be based on uncertain evidences and it is natural to consider that the α - and γ -positions in the glutaconic acids are not identical.⁽³⁾ Now that explanation

(1) This journal, 2 (1927), 281.

(2) Strictly speaking, they should not be called hydrates, for the water combined in those compounds can not be removed, showing that it is not the water of crystallisation.

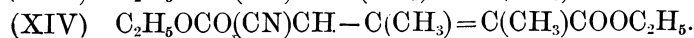
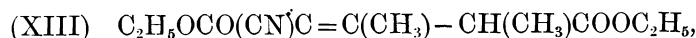
(3) This journal, 3 (1928), 205.

must be corrected according to this fact. In that and also in this paper it was shown that the condensation of $C_2H_5OCH=CXY$ with $CHNaX'Y'$, and the condensation of $C_2H_5OCH=CX'Y'$ with $CHNaXY$, where X, X', Y, and Y' represent any of the negative groups such as CN and $COOC_2H_5$, give one and the same product, while two with the following formulae can be expected :



Even a slight difference in the groups attached to each end of the propylene chain caused the seeming migration of the double union, only one compound free from the isomeride being produced in sufficient yield.

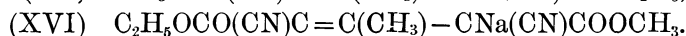
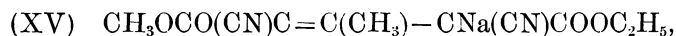
On the other hand, Hope⁽¹⁾ found clearly a difference between the two following derivatives of glutaconic acid :



He observed that the former is only very slowly transformed into the latter by the action of ammonia. By the action of sodium ethylate the former is also transformed into the sodium derivative of the latter, but only partly.

It may be supposed it is not impossible that the methyl group in the β -position of the compounds investigated by Hope prevented the double union from moving, and enabled the two isomerides to exist, and that, as there is no methyl group in the condensation product of an ethoxy-methylene compound with a sodio-methylene compound, the migration of the double union can easily take place.

But it has been found that this view is contradictory to the fact, for the condensation of methyl ethoxy-ethylidene-cyanoacetate with ethyl sodio-cyanoacetate and the condensation of ethyl ethoxy-ethylidene-cyanoacetate with methyl sodio-cyanoacetate gave the same product, while two corresponding to the following formulae are expected :



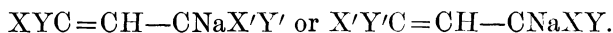
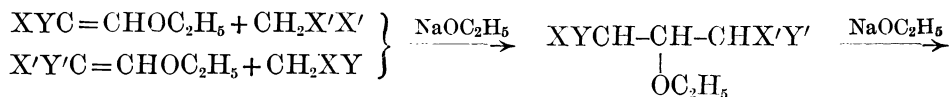
The details of the experiments will be given later in another paper.

Therefore, it is reasonable to suppose that the double union can not easily move after it has been once formed. Then how is the mechanism of the condensation in question explained? Suppose that an ethoxy-methylene compound and a methylene compound give, in the first place, an addition compound in the presence of sodium alcoholate, the elimination of alcohol and substitution of hydrogen with sodium taking

(2) *J. Chem. Soc.*, 121 (1922), 2216.

	Condensations	Sodium compounds obtained by the condensations	Compounds obtained by the action of an acid on the sodium compounds
(1)	$4\text{NaOMe} + 2\text{CH}_2(\text{CO}_2\text{Me})_2 + \text{CHCl}_3$	$(\text{MeO}_2\text{C})_2\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CO}_2\text{Me})_2$	$(\text{MeO}_2\text{C})_2\text{C}:\text{CH}\cdot$ $\text{CH}(\text{CO}_2\text{Me})_2$
(2)	$4\text{NaOEt} + 2\text{CH}_2(\text{CO}_2\text{Et})_2 + \text{CHCl}_3$		
(3)	$4\text{NaOEt} + 2\text{CH}_2(\text{CO}_2\text{Et})_2 + \text{CCl}_4$		
(4)	$4\text{NaOEt} + 2\text{CH}_2(\text{CO}_2\text{Et})_2$ $+ \text{Cl}_3\text{CCO}_2\text{Et}$	$(\text{EtO}_2\text{C})_2\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CO}_2\text{Et})_2$	$(\text{EtO}_2\text{C})_2\text{C}:\text{CH}\cdot$ $\text{CH}(\text{CO}_2\text{Et})_2$
(5)	$\text{NaOEt} + \text{CH}_2(\text{CO}_2\text{Et})_2$ $+ \text{EtOCH}:\text{C}(\text{CO}_2\text{Et})_2$		
(6)	$\text{NaOMe} + \text{CH}_2(\text{CO}_2\text{Me})_2$ $+ \text{EtOCH}:\text{C}(\text{CO}_2\text{Et})_2$	$\text{C}_{13}\text{H}_{17}\text{O}_8\text{Na}$	$\text{C}_{13}\text{H}_{15}\text{O}_8$
(7)	$\text{NaOEt} + \text{CH}_2(\text{CO}_2\text{Me})_2$ $+ \text{EtOCH}:\text{C}(\text{CO}_2\text{Et})_2$	$\text{C}_{14}\text{H}_{19}\text{O}_8\text{Na}$	$\text{C}_{14}\text{H}_{17}\text{O}_8$
(8)	$\text{NaOEt} + \text{CNCH}_2\text{CO}_2\text{Et}$ $+ \text{EtOCH}:\text{C}(\text{CO}_2\text{Et})_2$	$\text{EtO}_2\text{C}(\text{CN})\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CO}_2\text{Et})_2$	$\text{EtO}_2\text{C}(\text{CN})\text{C}:\text{CH}\cdot$ $\text{CH}(\text{CO}_2\text{Et})_2$
(9)	$\text{NaOEt} + \text{CH}_2(\text{CO}_2\text{Et})_2$ $+ \text{EtOCH}:\text{C}(\text{CN})\text{CO}_2\text{Et}$		
(10)	$\text{NaOEt} + \text{CH}_2(\text{CN})_2$ $+ \text{EtOCH}:\text{C}(\text{CO}_2\text{Et})_2$	$(\text{CN})_2\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CO}_2\text{Et})_2$	$(\text{CN})_2\text{C}:\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ $\text{H}_2\text{NCO}(\text{CN})\text{C}:\text{CH}\cdot$ $\text{CH}(\text{CO}_2\text{Et})_2$
(11)	$\text{NaOEt} + \text{CH}_2(\text{CO}_2\text{Et})_2$ $+ \text{EtOCH}:\text{C}(\text{CN})_2$		$(\text{H}_2\text{NCO})_2\text{C}:\text{CH}\cdot$ $\text{CH}(\text{CO}_2\text{Et})_2$
(12)	$4\text{NaOMe} + 2\text{CNCH}_2\text{CO}_2\text{Me} + \text{CHCl}_3$	$\text{MeO}_2\text{C}(\text{CN})\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CN})\text{CO}_2\text{Me}$	$(\text{C}_9\text{H}_8\text{O}_4\text{N}_2)_2\text{H}_2\text{O}$
(13)	$4\text{NaOEt} + 2\text{CNCH}_2\text{CO}_2\text{Et} + \text{CHCl}_3$		
(14)	$4\text{NaOEt} + 2\text{CNCH}_2\text{CO}_2\text{Et} + \text{CCl}_4$		
(15)	$4\text{NaOEt} + 2\text{CNCH}_2\text{CO}_2\text{Et}$ $+ \text{Cl}_3\text{CCO}_2\text{Et}$	$\text{EtO}_2\text{C}(\text{CN})\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CN})\text{CO}_2\text{Et}$	$(\text{C}_{11}\text{H}_{12}\text{O}_4\text{N}_2)_2\text{H}_2\text{O}$
(16)	$\text{NaOEt} + \text{CNCH}_2\text{CO}_2\text{Et}$ $+ \text{EtOCH}:\text{C}(\text{CN})\text{CO}_2\text{Et}$		
(17)	$\text{NaOEt} + \text{CNCH}_2\text{CO}_2\text{Me}$ $+ \text{EtOCH}:\text{C}(\text{CN})\text{CO}_2\text{Et}$	”	”
(18)	$\text{NaOMe} + \text{CNCH}_2\text{CO}_2\text{Me}$ $+ \text{EtOCH}:\text{C}(\text{CN})\text{CO}_2\text{Et}$	$\text{C}_{10}\text{H}_9\text{O}_4\text{N}_2\text{Na}$	$(\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_2)_2\text{H}_2\text{O}$
(19)	$\text{NaOEt} + \text{CNCH}_2\text{CO}_2\text{Et}$ $+ \text{EtOCH}:\text{C}(\text{CN})\text{CO}_2\text{Me}$		
(20)	$\text{NaOMe} + \text{CNCH}_2\text{CO}_2\text{Et}$ $+ \text{EtOCH}:\text{C}(\text{CN})\text{CO}_2\text{Me}$	$\text{MeO}_2\text{C}(\text{CN})\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CN})\text{CO}_2\text{Me}$	$(\text{C}_9\text{H}_8\text{O}_4\text{N}_2)_2\text{H}_2\text{O}$
(21)	$\text{NaOEt} + \text{CH}_2(\text{CN})_2$ $+ \text{EtOCH}:\text{C}(\text{CN})\text{CO}_2\text{Et}$	$(\text{CN})_2\text{C}:\text{CH}\cdot$ $\text{CNa}(\text{CN})\text{CO}_2\text{Et}$	$(\text{C}_9\text{H}_7\text{O}_2\text{N}_3)_2\text{H}_2\text{O}$
(22)	$\text{NaOEt} + \text{CNCH}_2\text{CO}_2\text{Et}$ $+ \text{EtOCH}:\text{C}(\text{CN})_2$		
(23)	$\text{NaOEt} + \text{CH}_2(\text{CN})_2$ $+ \text{EtOCH}:\text{C}(\text{CN})_2$	$(\text{CN})_2\text{C}:\text{CH}\cdot\text{CNa}(\text{CN})_2$	$(\text{CN})_2\text{C}:\text{CH}\cdot\text{CH}(\text{CN})_2$
(24)	$4\text{NaOEt} + 2\text{CH}_2(\text{CN})_2 + \text{CHCl}_3$	—	$(\text{C}_9\text{H}_8\text{ON}_4)_2\text{H}_2\text{O}$

place subsequently, then how two different condensations give the same product will be well understood.



The hydrogen in the carbon with less cyano-groups is substituted with sodium, while the hydrogen in the carbon with more cyano-groups is splitted off forming ethyl alcohol with the ethoxy-group.

Summary. The table shows the outlines of synthetical studies made by the present author and others in regard to the nitrile-esters of dicarboxy-glutaconic acid. The water of crystallisation which is present in some of the sodium compounds is omitted. The configurations of those written in molecular formulae are not yet known. As to the constitution of those written in the formula $(\dots)_2\text{H}_2\text{O}$, see this journal, **2** (1927), 29. The details will be found in the following places :

- (1) Guthzeit, Weiss and Schoefer, *J. prakt. Chem.*, **80** (1909), 439.
- (2) Conrad, Guthzeit, *Ber.*, **15** (1882), 2842; *Ann.*, **222** (1884), 250.
- (3) Zelinsky, Doroschewsky, *Ber.*, **27** (1894), 3374; Bischoff, *Ber.*, **28** (1895), 2829.
- (4)' Ruhemann, *Ber.*, **29** (1896), 1017.
- (5) Claisen, Haase, *Ann.*, **297** (1897), 88.
- (6), (7) Urushibara, this journal, **3** (1928), 220.
- (8), (9) Errera, *Ber.*, **31** (1898), 1243; Urushibara, this journal, **2** (1927), 280; **3** (1928), 223.
- (10), (11) Urushibara, this journal, **2** (1927), 281.
- (12) Urushibara, this journal, **2** (1927), 240.
- (13) Errera, *Ber.*, **31** (1898), 1241; Ruhemann, Browning, *J. Chem. Soc.*, **73** (1898), 282; Urushibara, this journal, **2** (1927), 28, 236.
- (14) Dimroth, *Ber.*, **35** (1902), 2882.
- (15) Urushibara, this journal, **2** (1927), 237.
- (16) Urushibara, this journal, **2** (1927), 240, 283.
- (17), (18), (19), (20) Urushibara, this journal, **3** (1928), 219.
- (21), (22) Urushibara, this journal, **2** (1927), 284.
- (23) Urushibara, this journal, **2** (1927), 285.
- (24) Zörnig, *J. prakt. Chem.*, **74** (1906), 435.

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ON THE BASIC NITROGEN COMPOUNDS FROM
FUSHUN SHALE TAR. II.⁽¹⁾

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It is very clear, from the previous paper,⁽²⁾ that the light fraction from Fushun shale tar, consists, for the greater part, of the basic compounds of the pyridine series, being rich in the α and γ alkyl derivatives. A complete chemical examination should be made of the bases in order to get more precise knowledge of the constituents, and to find more satisfactory data on the constants of the pyridine bases by isolating them in a state of purity, since the data which have been reported for these compounds are often regarded as contradictory in their discordancies, and many even of the simple derivatives are still left awaiting identification, notwithstanding, that a great deal of work in that field has been set forth in the literature.⁽³⁾

4-Methylpyridine. The presence of 4-methylpyridine in coal tar has already been recognized by K. E. Schulze,⁽⁴⁾ A. Ladenburg,⁽⁵⁾ O. Flaschner,⁽⁶⁾ and many others but the fact seems to have been left alone by workers on the shale tar bases. The procedure followed in the preparation of this base has been, as in the case of other lower members of pyridine series, generally carried out by first refining the characteristic double salts of mercury or zinc-chloride, and then by regenerating and drying the free base. The mercuric chloride-method, however, includes much difficulty in the separation of the 3- and 4-methylpyridines in their fractions, for no marked features which might be utilised in such a practice, are recognized between them. Attempts were made to isolate 4-methylpyridine from the mixture of 2:6-dimethyl, 3-, and 4-methylpyridines by the aid of mercuric chloride but proved unsuccessful so far as the writer's experiments were concerned.

The base was accordingly treated successively with an insufficient amount of picric acid in alcohol, the crystallization being performed in a

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- (1) Contribution from the Scientific Research & Experimental Branch, Imperial Naval Fuel Depot, No. 2.
 - (2) This journal, **2** (1927), 176.
 - (3) V. Meyer & P. Jacobson, "Lehrbuch d. organ. Chem.", II, 3, p. 782-1047; N. V. Sidgwick, "The Organic Chemistry of Nitrogen", (1910); P. E. Spielmann, "The Constituents of Coal Tar", (1924); R. H. McKee, "Shale Oil", (1925); C. Hollins, "The Synthesis of Nitrogen Ring Compounds", (1924); A. R. Warnes, "Coal Tar Distillation and Working up of Tar Products", (1923).
 - (4) *Ber.*, **20** (1887), 411.
 - (5) *Ibid.*, **21** (1888), 287.
 - (6) *J. Chem. Soc.*, **95** (1909), 668.

thermostat with very great caution. Three kinds of picrate were formed ; (1) a dark yellow rhombic thick plate, m.p. 160° – 162° , (2) a light yellow thin plate, m.p. about 155° , (3) a dark yellow prism, m.p. about 125° , which appeared in the last stage. On recrystallizing the picrate (2) from boiling alcohol, flat needles, gathering in tufts, grew to several mm. in length showing a m.p. of 165° ; 44 gr. of the picrate again recrystallized from 600 c.c. of boiling ethyl alcohol, 41 gr. of a very slender prism with a m.p. of 167° resulted, which remained constant after further recrystallization. The base regenerated from 40 gr. of the purified picrate was dried over fused potash. yield 10.9 gr.

The base resembles 2:4-dimethylpyridine in odour, and is completely miscible with water at room temperature. It distils completely at 145.45° – 145.47° under 763.9 mm. The physical constants are ; $d_4^{25}=0.9502$ (in vac.) ; $n_D^{25}=1.5029$; $n_C^{25}=1.4986$; $n_F^{25}=1.5143$; $n_G^{25}=1.5240$.

0.1115 Gr. subst. gave 0.0756 gr. H_2O & 0.3165 gr. CO_2 . 0.1753 Gr. subst. gave 22.5 c.c. N_2 at 18° & 761 mm. (Found : C=77.42; H=7.59; N=15.08. C_6H_7N requires C=77.36; H=7.58; N=15.05 %)

The base was identified as 4-methylpyridine from its oxidation product being proved to be isonicotinic acid ; 1.7 gr. of the base was oxidised with 6 gr. of potassium permanganate ; the filtrate from manganese oxide was treated with copper acetate after being neutralised with dilute sulphuric acid and 1.7 gr. of a blue microscopic crystalline powder deposited. Analysis shows : Found : C=38.09; H=4.53; Cu=16.69. $(C_5H_4N CO_2)_2Cu \cdot 4H_2O$ requires C=37.92; H=4.25; Cu=16.74 %.

The free acid from the salt, recrystallized from water, has a m.p. of 315° when rapidly heated, but all sublimes without melting when slowly heated in a capillary. It has no colour reaction with ferrous sulphate.

0.1055 Gr. free acid gave 0.0395 gr. H_2O & 0.2256 gr. CO_2 . (Found : C=58.32; H=4.19. $C_6H_4N \cdot COOH$ requires C=58.51; H=4.10 %).

Some salts of the base were examined : $C_6H_7N \cdot HCl \cdot AuCl_3$ —slightly sol. in cold, but moderately in hot water, m.p., 218° ; $C_6H_7N \cdot HCl \cdot 2HgCl_2$ —needles; m.p., 130° .

3-Methylpyridine. 3-Methylpyridine is a possible constituent of various kinds of tar bases and has many records of being isolated⁽¹⁾ from them and synthesised.⁽²⁾

In view of the observations made during the investigation, mercuric

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- (1) H. Weidel, *Ber.*, **12** (1879), 2008 ; J. Mohler, *ibid.*, **21** (1888), 1009; O. Flaschner, *J. Chem. Soc.*, **95** (1909), 668 ; J. G. Heap, W. I. Jones & J. G. Speakman, *J. Am. Chem. Soc.*, **43** (1921), 1936.
 (2) E. Zandoni, *Ber.*, **15** (1882), 528 ; L. Storch, *ibid.*, **19** (1886), 2456; P. Schwarz, *ibid.*, **24** (1891), 1676.

chloride is not recommendable for isolation of the base in a pure state, as is the case with γ -picoline, because the work does not always prove successful. The purification, therefore, was carried out as in the preceding experiment with picrate.

The melting-point of picrate (3) written in the former section was raised to 149° by repeated crystallizations in alcohol, which in total, amounted to 41.5 gr.

The base regenerated and dried over fused potash was 11.3 gr. It has somewhat a sweetish odour and completely distils at 144.17°–144.18° under 763.0 mm. pressure, and shows $d_4^{25}=0.9518$ (in vac.); $n_D^{25}=1.5038$; $n_C^{25}=1.4994$; $n_F^{25}=1.5155$; $n_G^{25}=1.5256$.

It yields the following double salts with metallic chlorides:

$(C_6H_7N \cdot HCl)_2PtCl_4$,	m.p., 208°.
$C_6H_7N \cdot HCl \cdot AuCl_3$,	a pale yellow fibre, melts at 187°.
$C_6H_7N \cdot HCl \cdot HgCl_2$,	long needles melting at 145°–146°.
$C_6H_7N \cdot HCl \cdot 2HgCl_2$,	m.p., 146°.
$C_6H_7N \cdot HCl \cdot 3HgCl_2$,	produced when treated with excess of $HgCl_2$, white granular crystalline with a m.p., 170°.

The base was proved to be 3-methylpyridine by the analysis of the base and its oxidation products, as follows:

0.1025 Gr. base gave 0.0700 gr. H_2O & 0.2901 gr. CO_2 . 0.1851 Gr. base gave 23.6 c.c. N_2 at 17° & 761 mm. (Found: C=77.19; H=7.65; N=15.04. C_6H_7N requires C=77.36; H=7.58; N=15.05%).

The base (1.4 gr.) was oxidised with the calculated amount of potassium permanganate (5 gr.); the free nicotinic acid crystallizes from hot water in a white mass, has no colour reaction with ferrous sulphate, partly, sublimes without decomposition and has a m.p. of 236°.

0.1050 Gr. subst. gave 0.2250 gr. CO_2 , & 0.0397 gr. H_2O . (Found: C=58.44; H=4.23. Theory: C=58.51; H=4.10%).

The copper salt was a bright blue crystalline powder, and gave on analysis,

C=45.83; H=2.78; Cu=20.77. $(C_6H_4N \cdot CO_2)_2 \cdot Cu$ requires C=46.81; H=2.62; Cu=20.66%.

2:3-Dimethylpyridine. F. C. Garrett and J. A. Smythe⁽¹⁾ have already proved the existence of this base in Scottish shale oil by isolating it with the aid of mercuric chloride in a certain grade of purity.

The method of procedure described in their report, however, is not appropriate in this case for getting it free from other isomers such as 2:5-dimethylpyridine, etc., owing to difficulty in obtaining it in a definite form

(1) *J. Chem. Soc.*, 81 (1902), 449; 83 (1903), 763.

with mercuric chloride. The picric acid method, in this respect, is superior to the mercuric chloride method in handling such bases.

The procedure for the isolation of this base from the fraction, b.p. 158°–160°, in which 2:4-lutidine and 2:6-collidine had been found, is briefly described below.

The fraction was dissolved into ten parts of hot alcohol. It yielded immediately a light yellow crystalline powder on adding picric acid dissolved in hot alcohol; and next, with some picric acid, gave partly the same crystals and partly flat needles. The former picrate has a m.p. of 188° after recrystallization from an excess of boiling alcohol. The free base regenerated from the picrate is a colourless liquid with a faint characteristic odour, soluble in 10 parts of water at 23°. It completely distils at 160.7° under 760 mm. The constants are: $d_4^{25}=0.9419$; $n_D^{25}=1.5057$; $n_C^{25}=1.5014$; $n_F^{25}=1.5172$; $n_{G_r}^{25}=1.5272$.

It was identified as 2:3-dimethylpyridine by analysis and by converting into quinolinic acid by oxidation.

0.1794 Gr. of the base gave 20.4 c.c. N_2 at 25° 0 & 762 mm. (Found: $N=13.05$. C_7H_9N requires $N=13.08\%$).

It yields a double salt with mercuric chloride, $C_7H_9N \cdot HCl \cdot 6HgCl_2$ m.p. 194°.

The acid obtained in a free state from its copper salt shows an orange-red colour with ferrous sulphate, and a m.p. of 247° when slowly heated in a capillary, but by rapid heating sinters at about 190° and then melts at 233°.

0.1385 Gr. subst. gave 0.0386 gr. H_2O & 0.2575 gr. CO_2 . (Found: $C=50.71$; $H=3.12$. Theory: $C=50.28$; $H=3.02\%$).

2:5-Dimethylpyridine.⁽¹⁾ During the course of the fractional crystallization, shown in the foregoing section, the writer obtained flat needles, to a fair amount, after a powdery picrate of 2:3-dimethylpyridine had been removed, and this, on decomposing with an alkali, gave quite a different odour from those of the dimethylpyridines described above, but rather resembling that of β -picoline, which in connection with the odours of the β -methylpyridines affords some idea, that it might be 2:5-dimethylpyridine.

Twenty three grams of the pure salt, with a m.p. of 167° obtained by repeating the recrystallization from hot alcohol, yielded 5 gr. of the free base.

It is a colourless liquid with a sweetish odour, less pungent than β -picoline. It boils constantly at 156.82°–156.88° under 759.1 mm. and is soluble in 12 parts of water at 23°. The physical constants are: $d_4^{25}=0.9261$ (in vac.); $n_D^{25}=1.4982$; $n_C^{25}=1.4939$; $n_F^{25}=1.5095$; $n_{G_r}^{25}=1.5194$.

(1) G. Lunge & J. Rosenberg, *Ber.*, **20** (1887), 134; F. C. Garrett, & J. A. Smythe, *J. Chem. Soc.*, **81** (1902), 453.

It yields the salts: $(C_7H_9N \cdot HCl)_2PtCl_4$ (214°); $C_7H_9N \cdot HCl \cdot 6HgCl_2 \cdot H_2O$ (203°).

The base was noticed to be the same compound as the 2:5-dimethylpyridine, which were synthesised by G. Errera,⁽¹⁾ and for confirmation it was analysed and then oxidized by the usual method to isonicotinic acid.

0.1071 Gr. subst. gave 0.0826 gr. H_2O & 0.3070 gr. CO_2 . 0.1838 Gr. subst. gave 20.6 c.c. N_2 at 21° & 763 mm. (Found: C=78.18; H=8.64; N=13.07. C_7H_9N requires C=78.45; H=8.47; N=13.08%).

The free acid recovered from the copper salt of pale blue colour, is almost insoluble in cold water, slightly in hot, but more soluble in hot hydrochloric acid. When recrystallized from dilute hydrochloric acid it melts at 254°, while from boiling alcohol, it melts at 238° (with decomposition).

The free acid on analysis, responded as a pyridine-dicarboxylic acid with one mol of the water of crystallization.

0.1129 Gr. of the free acid lost 0.0105 gr. on drying. 0.1024 Gr. of the dried acid gave 0.0295 gr. H_2O & 0.1869 gr. CO_2 . (Found: C=49.78; H=3.23; combined water=9.30. $C_7H_5O_4N \cdot (H_2O)$ requires C=50.27; H=3.02; combined water=9.74%).

3:5-Dimethylpyridine.⁽²⁾ The presence of 3:5-dimethylpyridine in a coal tar base, has already been proved by F. B. Ahrens⁽³⁾ and his co-workers.

The writer has also succeeded in isolating it, with the aid of picric acid, from the fraction b. p. 170°–172° of shale tar base in a pure state. The base which was isolated from the picrate has a faint odour somewhat resembling horse urine and β -picoline. The physical constants of the dried base are: b. p. 171.6° (760 mm.); $d_4^{25}=0.9385$; $n_D^{25}=1.5032$; $n_C^{25}=1.4988$; $n_F^{25}=1.5146$; $n_G^{25}=1.5244$.

0.1033 Gr. subst. gave 0.0771 gr. H_2O & 0.2964 gr. CO_2 . (Found: C=78.37; H=8.36. C_7H_9N requires C=78.45; H=8.47%).

The base yields by oxidation, nicotinic acid which melts at 327°.

0.1097 Gr. subst. gave 0.2016 gr. CO_2 & 0.0313 gr. H_2O . (Found: C=50.12; H=3.19. $C_7H_5O_4N$ requires C=50.28; H=3.02%).

3:4-Dimethylpyridine. In view of certain relations between the chemical structure of compounds and their physical constants being symphonious, the data exhibited by the series of pyridine homologues which the writer has isolated in a highly pure state, are likely to be of value in affording excellent examples, especially in offering a distinct regularity displayed by the boiling points; that is, if the hydrogen atom combined with the α -position of pyridine is replaced by a methyl group, the rise of the boiling-point is approxi-

(1) G. Errera, *Ber.*, **34** (1901), 3691.

(2) E. Dürkopf & H. Gottsch, *Ber.*, **23** (1890), 1113.

(3) *Ibid.*, **37** (1904), 2064.

mately one-half as compared with that of the β or γ -methyl derivative. 3:4-Dimethylpyridine, which is the only one left awaiting identification among the theoretical dimethylpyridines, as the others have been already isolated in a pure state by the writer, was discovered by pursuing it in the fraction of b.p. 178°–180°, with the expectation that the boiling point would not be lower than that of 3:5-dimethylpyridine, though we find it lower than that in the literature.⁽¹⁾

The fractions boiling at 177°–178° (25 gr.) and at 178°–179° (30 gr.) were treated with the calculated amount of picric acid in boiling methyl alcohol and slowly cooled, producing three kinds of crystals, which separated mechanically into

- (1) upper crop of needles or prisms, m.p. 114°,
- (2) middle crop of aggregates of small needles, m.p. 120°–140°, and
- (3) bottom crop of prisms, m.p. about 163°.

The picrate which has a m.p. of about 163° was the main product in each case, and 19.4 gr. of the pure salt of m.p. 163° by recrystallizing twice from methyl alcohol were obtained.

The free base is a colourless liquid with a faint aromatic odour, soluble in 20 parts of water at 22°, and distilling completely at 178.82° under 759 mm., and yields the following salts:

$(C_7H_9N \cdot HCl)_2PtCl_4$,	orange-red prism, m.p. 276° (decomp.)
$C_7H_9N \cdot HCl \cdot 3HgCl_2 \cdot 2H_2O$,	slender needles, easily soluble in hot, but only slightly in cold water, (Hg. found 60.66; theory 60.72; m.p. 130.5°–131°)
$C_7H_9N \cdot HCl \cdot AuCl_3$,	fern-like crystals, m.p. 187°.

It gave the constants: $d_4^{25} = 0.9537$ (in vac.); $n_D^{25} = 1.5099$; $n_C^{25} = 1.5055$; $n_F^{25} = 1.5209$; $n_G^{25} = 1.5305$.

The base was identified as 3:4-dimethylpyridine, by analysis of the base and also by the oxidation to cinchomeronic acid with a m.p. of 265°–266°.

0.1016 Gr. of the base gave 0.0766 gr. H_2O & 0.2920 gr. CO_2 . 0.1512 Gr. of the base gave 17.6 c.c. N_2 at 24° & 758 mm. (Found: C=78.38; H=8.44; N=13.09; mol. wt.=108.6. C_8H_9N requires C=78.45; H=8.47; N=13.08%; mol. wt.=107.1).

0.1081 Gr. of the free acid gave 0.0306 gr. H_2O & 0.1997 gr. CO_2 . (Found: C=50.38; H=3.17. $C_5H_3N \cdot (CO_2H)_2$ requires C=50.28; H=3.02%.)

2:4-Methyl-ethylpyridine.⁽²⁾ In the fraction of 178°–180°, the writer has found 2:4-methylethylpyridine presumably together with 2:6-parvoline from an amorphous picrate.

The fraction, which removed 3:4-dimethylpyridine etc. by means of

(1) *Ber.*, **29** (1896), 2996.

(2) H. Weidel & B. Pick, *Ber.*, **18** (1885), Ref. 117; M. Schultz, *ibid.*, **20** (1887), 2720.

picric acid in alcohol, consisted mostly of a base forming an oily picrate. The oily picrate contaminated with crystalline picrates was separated mechanically from the latter after standing in an open vessel for six months in a dark and cool place.

The base recovered from the oily picrate was about a half of the original sample in the fraction of 178° – 180° , and is a colourless liquid with a highly disagreeable odour incomparable to those of the methylpyridines, and soluble in water to a slight degree. The constants are: b.p. = 179° – 180° ; d_4^{25} = 0.9130; n_D^{25} = 1.4953.

The main portion of the base was considered to be 2:4-methylethylpyridine on the whole, as it was oxidised to a lutidinic acid with a m.p. of 246° , though the results of combustion and mean molecular weight determination slightly exceeded the values for collidine.

Found: C = 79.42; H = 9.37; mol. wt. = 126. C_7H_9N requires C = 79.27; H = 9.16%; mol. wt. = 121.

Found: C = 45.03; H = 3.96. $C_7H_5O_4N \cdot H_2O$ requires C = 45.39; H = 3.81%.

2:3:6-Trimethylpyridine. If an idea which is based on the fact that the methyl group attached to the carbon atoms of the pyridine nucleus has some definite effects upon the boiling points of the methyl derivatives of pyridine, be extended to the higher members of the series, the boiling point of 2:3:6-trimethylpyridine would be considered to stand near with that of 2:4:6-trimethylpyridine which is the main constituent in the fraction b.p. 170° – 172° . The attempt, therefore, was advanced to find it out in that fraction which, after the most of the 2:4:6-trimethylpyridine had been removed with mercuric chloride, was found to consist of a mixture of the bases when they were regenerated from the double salts. The bases which were recovered from the salts were colourless liquids with highly disagreeable odour which produced three kinds of crystalline picrates on treating them successively with an insufficient amount of picric acid in alcohol, viz.,

- (1) light yellow needles of 2:4:6-trimethylpyridine picrate, m.p. 156° ,
- (2) a powdery picrate of 3:5-dimethylpyridine with a m.p. of 241° ,
- (3) a large hexahedron, orange in colour, easily crystallizable from alcohol, m.p., about 147° , with a yield of 48 gr.

The third picrate was purified twice from boiling methyl alcohol, yielding 41 gr. of the salt with a m.p. of 147° – 148° .

The base regenerated from the salt by usual method and dried over fused potash, boils at 172.88° – 172.90° under 761.2 mm., and is soluble in 32 parts of water at 26° .

The constants are: d_4^{25} = 0.9220 (in vac.); n_D^{25} = 1.5018; n_C^{25} = 1.4976; n_F^{25} = 1.5133; n_G^{25} = 1.5232.

It gave the following salts :

$C_8H_{11}N \cdot HCl \cdot AuCl_3$,	scales or needles, m.p. 139°,
$(C_8H_{11}N \cdot HCl)_2PtCl_4$,	blackens from about 220°,
$C_8H_{11}N \cdot HCl \cdot 2HgCl_2 \cdot H_2O$,	a slender prism, m.p. 104° (Hg. found, 56.3; theory, 55.8%),
$C_8H_{11}N \cdot HCl \cdot 6HgCl_2$,	white granular crystals, m.p. 165° (Hg. found, 66.7; theory, 66.7%).

For identification it was analysed with the following results :

0.1118 Gr. of the base gave 0.0918 gr. H_2O & 0.3247 gr. CO_2 . 0.1947 Gr. of the base gave 19.7 c.c. N_2 at 25° & 759 mm. (Found : C=79.21 ; H=9.19; N=11.58. $C_8H_{11}N$ requires C=79.27 ; H=9.16 ; N=11.50%).

The acid obtained from the base by oxidation with a potassium permanganate solution is extremely soluble in water, and shows a deep orange-red colouration with ferrous sulphate, which on neutralizing with a dilute sodium carbonate solution changes to a beautiful carmine-red. It melts at 245° with decomposition and agrees with 2:3:6-pyridinetricarboxylic acid written in the literature.⁽¹⁾

(To be continued on next page)

(1) L. Weiss, *Ber.*, 19 (1886), 1305.

ON THE BASIC NITROGEN COMPOUNDS FROM FUSHUN SHALE TAR. II.

By Takashi EGUCHI.

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(Continued from the last page).

2:3:5-Trimethylpyridine. The writer has succeeded in isolating 2:3:5-trimethylpyridine, a new base, as one of the chief constituents in the fraction of 186°–190°, which has never been before submitted to a satisfactory investigation and forms the sixth upheaval in the fractionation curve, (cf. previous report p. 179).

The fraction (71 gr.) was treated with the calculated amount of picric acid, in an alcohol solution, and the crystalline picrate was collected, and yielded 30 gr. of the free base. The base was again treated with an insufficient quantity of picric acid in an excess of alcohol out of which the picrate was produced in the form of cilia first which melts at 184° after purification.

Twenty one gr. of the purified picrate gave 6.8 gr. of the base with a faint agreeable odour resembling 3:5-dimethylpyridine in a way. The boiling point of the dried base over fused potash remained constant during the distillation at 186.75° (761.1 mm.).

The constants are ; $d_4^{25} = 0.9310$ (in vac.) ; $n_D^{25} = 1.5057$; $n_C^{25} = 1.5014$; $n_F^{25} = 1.5171$; $n_D^{25} = 1.5270$.

$(C_8H_{11}N \cdot HCl)_2PtCl_4$ an orange-red prism, m.p. 212°. (0.1032 Gr. subst. gave 0.0297 gr. Pt. Found Pt=28.8, theoretical Pt=28.7%).

$C_8H_{11}N \cdot HCl \cdot 3HgCl_2$ needles ; soluble in hot, slightly in cold water ; m.p. 110°.

Picrate a needle from hot alcohol ; slightly soluble even in hot alcohol.

0.1016 Gr. base gave 0.0830 gr. H_2O and 0.2954 gr. CO_2 . 0.1872 Gr. base gave 19.3 c.c. N_2 at 26° and 757 mm. (Found : C=79.29 ; H=9.15 ; N=11.73. $C_8H_{11}N$ requires C=79.27 ; H=9.16 ; N=11.56 %).

1.3 Gr. of the base was oxidised with potassium permanganate and the oxidation product was purified as a silver salt, and decomposed with hydrogen sulphide, yielding 1.5 gr. of the free acid.

The free acid is easily soluble in hot water, but not in cold, crystallizes out from water as white granules ; melts at 320°–322° with decomposition, and becomes deep orange-red with ferrous sulphate. The analysis and

properties of the free acid agree well with those of 2:3:5-pyridinetri-carboxylic acid.⁽¹⁾

0.1452 Gr. free acid lost 0.0200 gr. on drying at 110° for 2 hours. To neutralise 0.1013 gr. of free acid required 12.5 c.c. of N/10 NaOH using phenolphthalein as indicator. 0.1127 Gr. dried acid gave 0.0290 gr. H₂O and 0.1862 gr. CO₂. (Found: water of crystallization=13.77; C=45.06; H=2.88; mol. wt.=243. C₆H₂N·(CO₂H)₃·2H₂O requires water of crystallization=14.58; C=45.49; H=2.39%; mol. wt.=247).

2:4:5-Trimethylpyridine.⁽²⁾ In view of a certain relationship among the boiling-points of the methyl-pyridines which was stated above, we can assume that among the trimethylpyridines, 2:3:4-, 2:3:5-, and 2:4:5-methyl pyridines would exist in the fraction of b. p. 186°–190°, and the last two substances have been isolated.

By treating the fraction with picric acid 2:3:5-collidine was separated out in ciliform-like crystals (cf. former section) and then, the scaly crystals of 2:4:5-trimethyl pyridine appeared polluted by the former, which transformed gradually into thick plates in alcohol and could be readily separated from the latter mechanically by decantation. The melting-point of the picrate, on purifying from the alcohol solution, showed constant at 161° and the yield was 29 gr.

The base has a characteristic odour like the kidney-bean, and is soluble in 50 parts of water at 25°. The dried base completely distils at 190.04°–190.05° under 766.1 mm. and has the constants: $d_4^{25}=0.9330$ (in vac.); $n_D^{25}=1.5054$; $n_C^{25}=1.5013$; $n_F^{25}=1.5165$; $n_G^{25}=1.5260$.

(C₈H₁₁N·HCl)₂PtCl₄ needles, m.p. 192°

C₈H₁₁N·HCl·3HgCl₂·2H₂O . . glass-wool-like needles, m.p. 112° (Hg found=59.5; theory=59.7%)

0.1067 Gr. of the base gave 0.0875 gr. H₂O and 0.3107 gr. CO₂. 0.1900 Gr. base gave 19.3 c.c. N₂ at 25° and 759 mm. (Found: C=79.42; H=9.18; N=11.63; mol. wt.=121. C₈H₁₁N requires C=79.27; H=9.16; N=11.56%; mol. wt.=121.1).

The base (1.2 gr.), on oxidation with potassium permanganate solution yielded 1.6 gr. of free acid (m.p. 244°) which was ascertained to be "berberonic acid"⁽³⁾ from its form, solubility in water and colour reaction toward ferrous sulphate.

To neutralise 0.1017 gr. of free acid required 12.2 c.c. N/10 NaOH. 0.1629 Gr. free acid lost 0.0221 gr. on drying at 96° for 3 hours. 0.1065 Gr. dried acid gave 0.0235 gr. H₂O and 0.1775 gr. CO₂. (Found: water of

(1) E. Dürkopf and M. Schlaugk, *Ber.*, **21** (1888), 835.

(2) F.B. Ahrens, *Ber.*, **29** (1896), 2999.

(3) O. Mumm and H. Hüneke, *Ber.*, **51** (1918), 150.

crystallization = 13.56; C = 45.46; H = 2.47; mol. wt. = 250. $C_6H_2N \cdot (CO_2H)_3 \cdot 2H_2O$ requires $H_2O = 14.58$; C = 45.49; H = 2.39%; mol. wt. = 247).

2:3:4:6-Tetramethylpyridine. It was assumed that the two isomers of tetramethylpyridine, (2:3:4:6- and 2:3:5:6-) would occur in the last fraction b.p. 200°–202°.

On treating the base of this portion with picric acid in an alcohol solution, crystalline and amorphous picrates were obtained. The amorphous picrate was extremely soluble even in cold alcohol, but only slightly in hot water, and this picrate on decomposition with alkali liberated a colourless base of a strong offensive odour. It was neutralised with a very dilute hydrochloric acid and when treated with picric acid, a brownish-red oily picrate was deposited, which on standing for a week or so, was gradually transformed into pale yellow fur-like crystals, and on being purified from a dilute methyl alcohol solution, the yield of pure picrate (m.p. 107°) was 18 gr.

The free base is a hygroscopic colourless liquid with a faint odour resembling 2:4:6-trimethylpyridine, and is soluble in 150 parts of water. Dried base completely distils at 203.9° under 771 mm. The constants are: $d_4^{25} = 0.9229$; $n_D^{25} = 1.5084$; $n_C^{25} = 1.5043$; $n_F^{25} = 1.5195$; $n_G^{25} = 1.5290$.

The base was proved to be 2:3:4:6-tetramethylpyridine in the following manner:

0.1027 Gr. base gave 0.0896 gr. H_2O and 0.2993 gr. CO_2 . 0.2066 Gr. base gave 18.9 c.c. N_2 at 24° and 762 mm. (Found: C = 79.48; H = 9.77; N = 10.49; mol. wt. = 137. $C_9H_{13}N$ requires C = 79.93; H = 9.70; N = 10.37%; mol. wt. = 135.1).

The base (1.04 gr.) was oxidised with 12 gr. of $KMnO_4$; the filtrate from the manganese oxide was concentrated into a small bulk, neutralised with dilute sulphuric acid and treated with a saturated solution of copper acetate. The resulting copper-salt was bluish-green in colour and was ascertained on analysis to be the neutral copper-salt of pyridine-tetracarboxylic acid.

0.1607 Gr. copper salt (dried at 100°) gave 0.0299 gr. H_2O , 0.1383 gr. CO_2 and 0.0549 gr. CuO . (Found: C = 23.46; H = 2.08; Cu = 27.29. $C_6HN \cdot (CO_2)_4 \cdot Cu_2 \cdot 4H_2O$ or $C_6HN \cdot (CO_2H)_4 \cdot 2Cu(OH)_2$ requires C = 23.99; H = 2.01; Cu = 28.24%).

The free acid is readily soluble in cold water. A drop of a ferrous sulphate solution on the free acid develops a deep violet colouration, while a dark reddish-purple colour appears when a drop of an acid solution was added inversely to the ferrous sulphate; sinters at about 190° and melts at 236° with decomposition: these results agree well with those of pyridine-2:3:4:6-tetracarboxylic acid.⁽¹⁾

(1) O. Mumm and H. Hüneke, loc. cit.

0.1155 Gr. free acid lost 0.0181 gr. on drying at 110° for 2 hours. 0.0971 Gr. dried acid gave 0.0204 gr. H_2O and 0.1471 gr. CO_2 . To neutralise 0.1002 gr. of dried acid required 14.8 c.c. of $\text{N}/10$ NaOH . (Found : $\text{C}=41.32$; $\text{H}=2.35$; water of crystallization= 15.7 . $\text{C}_6\text{HN}(\text{CO}_2\text{H})_4 \cdot 3\text{H}_2\text{O}$ requires $\text{C}=42.34$; $\text{H}=1.98$; water of crystallization= 17.6%).

2 : 6 : 4-Dimethyl-ethylpyridine.⁽¹⁾ The fractions b.p. 187° – 188° and b.p. 189° – 190° were treated with the calculated amount of picric acid in hot alcohol, the mother liquor which separated from the crystals, was left to stand for a long time in an open flask. The brownish-red syrupy picrate filtered from any solid matter which might have been contained in it, gave 20 gr. of free base. The base is a colourless liquid but taking a slight colouring on long exposure to the light, soluble in 160 parts of water at 23° , possesses a characteristic odour of α and γ -methyl-ethylpyridines. B.p.= 187.5 – 188.0 (758 mm.) ; $d_4^{25}=0.9089$; $n_D^{25}=1.4964$.

The base corresponds to a parvoline, on analysis, and the oxidation with KMnO_4 gives rise to a "trimestic acid" as will be seen from what follows, which compels one of the three side-chains to take an ethyl group. Naturally, we can consider two isomers of such a parvoline according to the position to which the ethyl group is attached, and a close identity in the properties is recognized with 2 : 6-dimethyl-4-ethylpyridine which may therefore be assumed to be the chief constituent of the fraction mentioned.

$(\text{C}_9\text{H}_{13}\text{N} \cdot \text{HCl})_2\text{PtCl}_4$ m.p. 203° (0.1006 gr. subst. gave 0.0290 gr. Pt. Pt found= 28.8 , theory= 28.7)

Analysis : 0.0974 gr. base gave 0.0840 gr. H_2O and 0.2850 gr. CO_2 . (Found : $\text{C}=79.79$; $\text{H}=9.65$. $\text{C}_9\text{H}_{13}\text{N}$ requires $\text{C}=79.93$; $\text{H}=9.70\%$).

The base (3.7 gr.) gave 1.0 gr. of free acid on oxidation with potassium permanganate, which becomes a violet-red with ferrous sulphate, and melts at 228° .

Analysis : 0.1296 gr. acid lost 0.0184 gr. on drying at 115° for 2 hours. 0.1000 Gr. dried acid gave 0.0217 gr. H_2O and 0.1660 gr. CO_2 . (Found : water of crystallization= 14.20 ; $\text{C}=45.28$; $\text{H}=2.43$. $\text{C}_6\text{H}_2\text{N} \cdot (\text{CO}_2\text{H})_3 \cdot 2\text{H}_2\text{O}$ requires water of crystallization= 14.58 ; $\text{C}=45.50$; $\text{H}=2.39\%$).

Dimethyl-ethyl-pyridine (2 : 3 : 6 ?) From the fraction b.p. 189° – 190° , a base was isolated by means of picric acid, which slightly differs from 2 : 4 : 6-parvoline in odour and physical constants. B.p.= 190° – 190.5° (764 mm.) ; $d_4^{25}=0.9107$; $n_D^{25}=1.4970$.

The base was subjected to partial oxidation to form methyl-ethyl pyridine carboxylic acid which yields by heating with soda-lime, a modicum of 2 : 6-methyl-ethyl-pyridine.

Analysis : 0.1068 gr. base gave 0.0928 gr. H_2O and 0.3120 gr. CO_2 .

(1) F. Engelmann, *Ann.*, **231** (1885), 44 ; *Ber.*, **19** (1886), Ref. 16.

0.1728 Gr. base gave 15.7 c.c. N_2 at 30° and 756 mm.. (Found : C=79.67 ; H=9.74 ; N=10.3 ; mol. wt.=136. $C_9H_{13}N$ requires C=79.93 ; H=9.70 ; N=10.37% ; mol. wt.=135.1).

When, however, the base was oxidized completely with potassium permanganate, an acid with a m.p. of 245° resulted, which agrees in all respects with 2 : 3 : 6-pyridine tricarboxylic acid.

0.1046 Gr. of the dried acid gave 0.0262 gr. H_2O and 0.1725 gr. CO_2 . (Found : C=44.98 ; H=2.80. $C_8H_5O_6N$ requires C=45.49 ; H=2.39%).

Pyridane. Seeking to find any other compound of the pyridine series such as 3 : 4 : 5-trimethyl pyridine in the last fraction (200° – 202°), the writer came upon a peculiar base, which on pursuit with careful examination, of the picrate, was unveiled unexpectedly to be a new and interesting base that has never been found in shale or coal tars, and it would be worthy of note in the sense that it might be a mother substance of the pyridane series.

The picrate crystallizes from an excess of hot alcohol in flat needles with a m.p. 181° , which was converted into a free base of a hygroscopic, colourless liquid, possessing a faint odour like that of 2 : 3-dimethylpyridine, and one part of the base is soluble in 40 parts of water at 25° . The yield of the base from 9.5 gr. of the salt was 3 gr. The dried base distils completely at 199.8° (761 mm.) and the constants are : $d_4^{25}=1.029$; $n_D^{25}=1.541$; $n_C^{25}=1.536$.

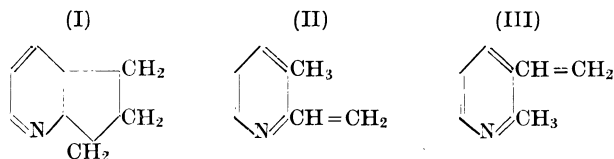
0.1210 Gr. and 0.1169 gr. base gave 0.0813 and 0.0800 gr. H_2O , and, 0.3561 and 0.3442 gr. CO_2 respectively. (Found : C=80.27 & 80.30 ; H=7.52 & 7.66 ; mol. wt.=121. C_8H_9N requires C=80.62 ; H=7.62% ; mol. wt.=119).

0.1124 Gr. and 0.1747 gr. $(B \cdot HCl)_2PtCl_4$ gave 0.0337 and 0.0522 gr. Pt respectively.

Oxidation of base ; 1.0 gr. of the base was oxidised with 9 gr. of potassium permanganate ; the acid formed by the oxidation was converted into a copper salt which showed the characteristic feature of copper quinolinite. The yield of quinolinic acid was 0.8 gr.

0.1048 Gr. free acid gave 0.0284 gr. H_2O and 0.1944 gr. CO_2 . (Found : C=50.17 ; H=3.03. $C_7H_5O_4N$ requires C=50.27 ; H=3.02%).

The structural formula for the base would eventually be settled in determining the manners in which the three carbon atoms combine together and are also attached to the pyridine ring :



From such a point of view the molecular refractivity was first examined. The value calculated from the experimental data shows $M_D=36.34$, while formula I will give $M_D=37.18$, II and III, $M_D=38.89$, in which the specific exaltation ΣE_D is calculated as -0.70 and -2.15 respectively, the latter being considered abnormal. The behavior of the base toward bromine being practically inert at room temperature, is favorable in supporting the structure (I) for the base, and moreover, considering the abnormality in density compared with that of the alkyl-pyridines and the behavior toward the oxidizing agent, such facts seem to compel formula II or III to be rejected.

Some considerations on the boiling-points of the methylpyridines. Although the effect of the methyl group on the boiling-points of certain homologous series, such as the hydrocarbons, alcohols, and acids has been studied by many investigators, there can be little doubt that it is impossible, as conjectured from the stereochemical view point, to contemplate such an attempt in the series of the methylpyridines with all the data hitherto given in the literature. But with the data which the writer has observed throughout the members many regular relations are recognized in them as already stated, if we ascend the series or among the isomers themselves. Convinced that the effect of the methyl group in α -position on the "boiling-point-rise" of the methylpyridines is about half of that of the β - or γ -position throughout the members, yet some anomalies are always found in connection with such members which have methyl groups successively attached unsymmetrically to the pyridine ring. If this is corrected by C the boiling points of the methylpyridines can be expressed by a fairly simple empirical formula, that is,

$$T=115.3^\circ + 14m + 28m' + C$$

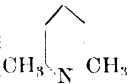
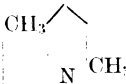
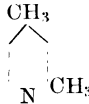
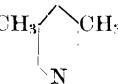
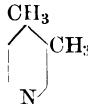
where T is a b.p. of methylpyridine, m the number of the α -methyl group m' the number of the β - or the γ -methyl group, and C the correction term.

The correction term C is variable with the position in the pyridine nucleus, by which the methyl groups connected, that is, 4° for the 2:3 (γ : β)-methyls, 8° for the 3:4 (β : γ), and these values are diminished to one half if two side-chains are situated in the 1:4 positions or para-position.

For the methyl derivatives of ethyl-pyridine, 115.3 (b.p. of pyridine) in the above formula should be replaced by the b.p. of ethylpyridine.

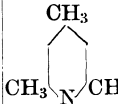
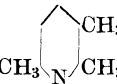
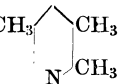
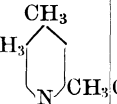
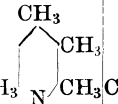
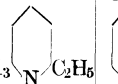
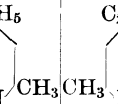
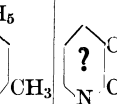
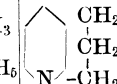
In the following table the results of such calculations are given with the author's experimental data in which slight corrections are made in order to compare them under 760 mm.

Physical Constants of Pyridine Series.

										
	N	N-CH ₃	N	N	CH ₃ -N-CH ₃	CH ₃ -N-CH ₃	N-CH ₃	N-CH ₃	N-CH ₃	N
B.p. (760 mm.)	115.3	129.3	144.0	145.3	144.0	157.0	158.0	160.8	171.6	178.9
	{obs.									
	{calc.									
d_4^{25}	0.9781	0.9400	0.9518	0.9502	0.9183	0.9261	0.9271	0.9419	0.9385	0.9537
n_D^{25}	1.5068	1.4983	1.5038	1.5029	1.4953	1.4982	1.4984	1.5057	1.5032	1.5099
n_C^{25}	1.5022	1.4939	1.4994	1.4986	1.4910	1.4939	1.4942	1.5014	1.4988	1.5055
n_F^{25}	1.5187	1.5097	1.5155	1.5143	1.5065	1.5095	1.5095	1.5172	1.5146	1.5209
$n_{G'}^{25}$	1.5290	1.5197	1.5256	1.5240	1.5164	1.5194	1.5190	1.5272	1.5244	1.5305
M_D	24.04	29.04	28.94	28.95	34.02	33.90	33.88	33.76	33.74	33.58
M_G	23.86	28.82	28.73	28.74	33.77	33.66	33.64	33.52	33.49	33.34
M_F	24.52	29.60	29.51	29.50	34.67	34.55	34.52	34.41	34.38	34.19
$M_{G'}$	24.93	30.09	30.00	29.97	35.24	35.12	35.06	34.96	34.93	34.72
D (G'-C)	1.07	1.27	1.27	1.23	1.47	1.46	1.42	1.44	1.44	1.38
D (F-C)	0.66	0.78	0.78	0.76	0.90	0.89	0.88	0.89	0.89	0.85
ΣE_D	-1.44	-0.90	-1.01	-1.00	-0.43	-0.54	-0.56	-0.67	-0.69	-0.84
Picrate (m.p.)	167	165	149	167	162	167	182	188	244	163
(B·HCl) ₂ PtCl ₄ (m.p.)	268	205	208	253	211	214	217		263	276
B·HCl·AuCl ₃ (m.p.)		181-2	186-7	218						187
B·HCl·(X)HgCl ₂ (m.p.)	(X) = (2) : 176	(2):153-4	(1):145-6 (2):146 (3):170	(2):130	(1):191.5 (2):167	(6):203	(2):131-2	(6):194		(3):131
Sol. in X pts. of water	any rate (20°)	any rate (20°)	any rate (20°)	any rate (20°)	any rate (20°)	12(23°)	11.5(35°)	10(23°)	32(23°)	20(22°)

Physical Constants of Pyridine Series.

(Continued.)

										
B.p. (760 mm.)	170.3	172.8	186.8	189.8	203.3	160-1	179-80	187.5-8.0	190-.5	199.8
d_4^{25}	0.9101	0.9220	0.9310	0.9330	0.9229	0.9207	0.9130	0.9089	0.9107	1.029
n_D^{25}	1.4959	1.5018	1.5057	1.5054	1.5084	1.4950	1.4953	1.4964	1.4970	1.541
n_C^{25}	1.4919	1.4976	1.5014	1.5013	1.5043	1.4908		1.4925		1.536
n_F^{25}	1.5069	1.5133	1.5171	1.5165	1.5195	1.5057		1.5071		
$n_{G'}$	1.5164	1.5232	1.5270	1.5260	1.5290	1.5151		1.5163		
M_D	38.86	38.75	38.62	38.52	43.34	38.36		43.46		
M_C	38.60	38.47	38.35	38.26	43.05	38.08		43.17		
M_F	39.59	39.50	39.35	39.24	44.14	39.06		44.25		
$M_{G'}$	40.22	40.14	39.98	39.84	44.81	39.67		44.92		
D (G'-C)	1.62	1.66	1.63	1.58	1.77	1.59		1.75		
D (F-C)	0.99	1.02	1.00	0.98	1.09	0.98		1.08		
ΣE_D	-0.18	-0.28	-0.38	-0.47	-0.26	-0.60		-0.17		
Picrate (m.p.)	157	148	184	161	107					
(B·HCl) ₂ PtCl ₄ (m.p.)	220	220	212	192						
B·HCl·AuCl ₃ (m.p.)		139								
B·HCl·(X)HgCl ₂ (m.p.)	(2):157	(2):104 (6):165	(3):110	(3):112						
Sol. in X pts. of water	34(20°)	38(26°)	66(20°)	50(25°)	150(28°)	55(30°)				

With the expectation that the constituents of the shale tar base boiling at 100°–200° must probably be the mixture of simple pyridine homologues such as the methyl or ethyl-pyridines, the writer has succeeded in isolating seventeen compounds of the pyridine series, three monomethyl pyridines, six dimethyl pyridines, four trimethyl pyridines, one tetramethyl pyridine, two methyl-ethyl-pyridines, one dimethyl-ethyl-pyridine in a highly pure state and in confirming that the theoretically possible isomers of the monomethyl, dimethyl and trimethyl derivatives occur in the shale tar as will be indicated in the table.

1st fraction	(128°–130°)		picoline (main).
2nd	„	(143°–145°)	 2:6-lutidine (main), 7 and 3-picolines.
3rd	„	(157°–160°)	 2:4-lutidine (main), 2:6-collidine, 2:3-and 2:5-lutidines.
4th	„	(170°–172°)	 2:4:6-collidine (main), 2:3:6-collidine, 3:5-lutidine (little).
5th	„	(178°–179°)	 3:4-lutidine, 2:4-collidine.
6th	„	(186°–190°)	 2:4:6-parvoline (main), 2:3:5-and 2:4:5-collidine, 2:3:6-parvoline.
7th	„	(200°–202°)	 2:3:4:6-parvoline, pyrindane.

Thus not only most of the constituents of the shale tar base boiling at 170°–200°, which had been left in the haziness of uncertainty in spite of all endeavours of many investigators, have been cleared up, but also consistent data throughout the members have been determined by rectifying some discrepancies which had crept into the literature.

Besides these pyridine bases, the writer has isolated a new base which has never before been synthesised nor yet isolated from any tars. The base, on analysis and examination of its physical and chemical properties is very likely to have the structure of a “Cyclopenteno-pyridine” and was called pyrindane from its close resemblance in its structure to indane as pyridine to benzene.

The writer desires to make grateful acknowledgment to Vice-Admiral G. Yamashita, Director of the Imperial Naval Fuel Depot, and Engineer Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch for promoting this investigation, and also to Professor S. Komatsu of the Kyoto Imperial University for his invaluable advice and encouragement in carrying out of this research.

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THE HELIUM CONTENTS AND THE AGES OF JAPANESE RADIO-ACTIVE MINERALS OCCURRING IN ISHIKAWA DISTRICT.

By Yoshihiko KANO and Bunnosuke YAMAGUCHI.

Received September 12, 1923. Published October 28, 1928.

It is well known that granted certain conditions of suitability, it is possible to calculate the age of a primary radioactive mineral from its contents of uranium, thorium and one of their disintegration end-products, i. e., lead or helium.

There occur in Ishikawa District, Japan, several kinds of radioactive minerals—ishikawaite,⁽¹⁾ samarskite, xenotime and monazite. A series of experiments has been undertaken to determine their contents of helium, from which the authors have calculated their ages. Determining the amount of lead in the ishikawaite, the authors have also estimated its maximum age⁽²⁾ and compared it with its minimum one calculated from the helium content.

Experimental.

The apparatus employed for the determination of helium is illustrated in Fig. 1. It is similar with that used by the authors for the measurement of helium in the natural gases of Japan,⁽³⁾ but the whole apparatus is constructed in a smaller size with some suitable modifications. A and B in Fig. 1 show the silica bulbs in which a sample of mineral is heated for the extraction of helium. A is used for dry heating and B for wet treatment of a sample.

As there is a fear of causing an appreciable error in the measurement of a small quantity of helium, if helium is absorbed by cocoanut charcoal cooled by liquid air even at reduced pressure, so the authors have made a preliminary experiment to determine the amount of helium absorbed by the charcoal in the bulb D.

Heating the bulb D to 300°C. by electric furnace, the whole apparatus is exhausted to a vacuum by an oil pump and further by the Töpler's pump F. After cooling of the bulb D, C and D are immersed in liquid air and a definite amount of helium is then introduced into the apparatus from the burette G. The experiment must be carried out with the same care as was

(1) A new kind of uranium mineral was found by Prof. Y. Shibata and named "ishikawaite". [*J. Chem. Soc. Japan*, **43** (1922), 648].

(2) E. Rutherford, "Radioactive Substances and their Radiations", (1913), p. 562, 599.

(3) *J. Chem. Soc. Japan*, **47** (1926), 13 & 452; *Report of the Aeronautical Research Institute, Tokyo Imperial University*, Vol. 1, No. 13 (1926).

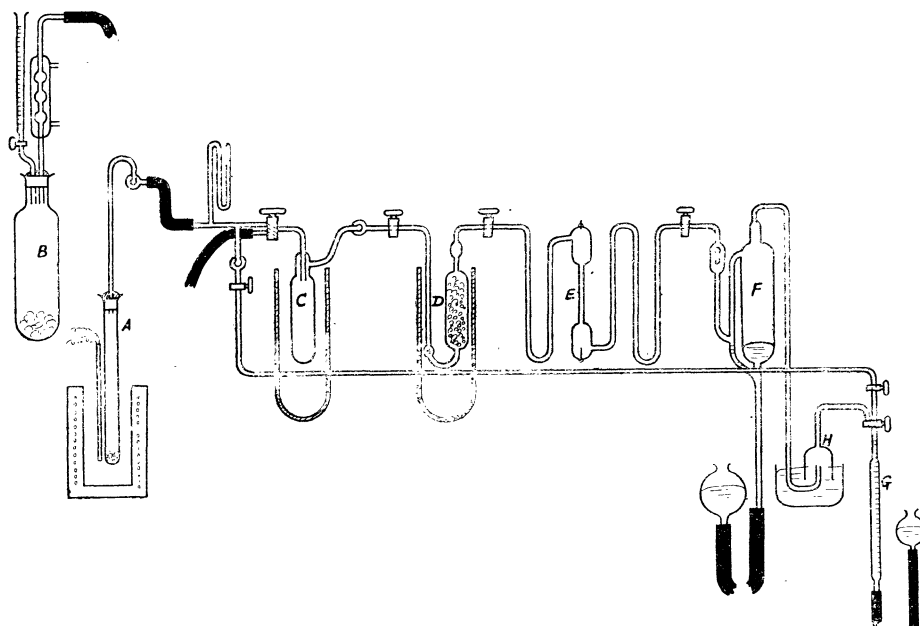


Fig. 1.

taken in the case of analysis of natural gases.⁽¹⁾ Lastly, the helium is drawn over into the adapter tube H by the Töpler's pump F. And as its quantity is measured by the burette G, the amount of helium absorbed by the charcoal in the bulb D can be calculated. Mc Lean⁽²⁾ observed in his experiment that the amount of helium absorbed by charcoal was so small that it was nearly independent on the quantities of helium introduced into the charcoal bulb. The result of the authors' experiment shown in Table 1, gives the same conclusion.

TABLE 1.

Reaction bulb	Helium introduced (c.c.)	Helium absorbed (c.c.)	Helium absorbed per gr. of charcoal (c.c.)
A (80 c.c.)	0.501	0.041	0.0018
	2.317	0.048	0.0021
	4.891	0.050	0.0022
B (400 c.c.)	0.565	0.038	0.0017
	2.293	0.049	0.0022
	4.812	0.056	0.0025

(1) loc. cit.

(2) *Trans. Roy. Soc. Canada*, 12, III (1918), 79.

Therefore, in the experiment for the determination of helium present in a radioactive sample, a small amount of helium is previously introduced into the apparatus and after a short time the apparatus is evacuated until no spark can be passed through the Plücker's tube E. And then, the sample being heated with or without a reacting agent, the helium is evolved and measured in the same manner as above. Powdered samples are used in all the experiments.

Helium in the Ishikawaite. The most radioactive mineral which, like the other minerals, has occurred in Ishikawa District accompanying smoky quartz, microcline and biotite in pegmatite layers, has been identified by means of chemical analysis with a mineral named "ishikawaite". It contains 20.86% uranium and 7.5% rare earth elements, possessing a specific gravity 6.3.

The amounts of helium liberated when the sample is heated at 1000°C. and when it is fused with acid potassium sulphate (one part of the sample and 8 parts KHSO_4) at 700°C. are given in Table 2, showing that the both methods give a concordant value.

TABLE 2.

Amount of mineral used (gr.)	Method of treatment	Heating temperature (°C.)	Heating duration (hours)	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
2.0013	Mere heating	1000°	2	3.551	1.77
2.0020	One part of the sample is fused with 8 parts of KHSO_4 .	700°	7	3.483	1.74

TABLE 3.

Amount of mineral used (gr.)	Heating duration at 700°C. (hours)	Helium evolved (c.c.)	Helium evolved per gr. of sample (c.c.)
2.0021	$\frac{1}{2}$	3.229	1.613
1.9999	1	3.346	1.673
1.0015	$1\frac{1}{2}$	1.701	1.698
2.0005	2	3.448	1.723
2.0000	4	3.465	1.733
2.0020	8	3.483	1.740

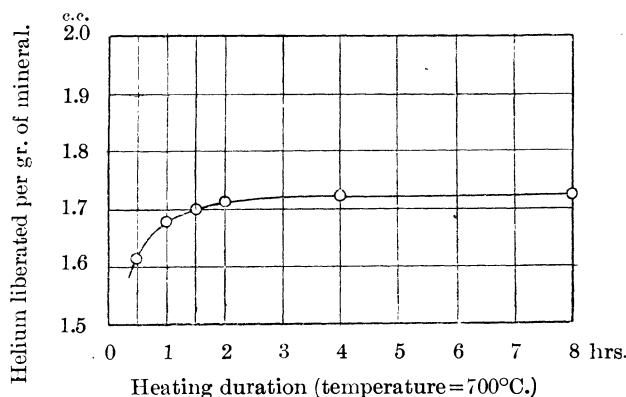


Fig. 2.

Table 3 and Fig. 2 show the effect of heating duration on the liberation of helium when the sample is fused at 700°C. with the same amount of KHSO_4 as itself. It is seen that the gas is emitted almost completely after four hours' fusing. If the heating temperature is raised more than 700°C., the rate of liberation of helium increases. This is evident from the results shown in Fig. 3 and Table 4. For the deficiency of the pure sample of ishikawaite, it has been obliged to use a sample somewhat mixed with columbite in this case. The sample contains 14.26% UO_2 . Curve I gives the amounts of helium emitted by mere heating of the sample for two hours at various temperatures. On red heat (700–800°C.) the gas in the mineral is liberated nearly by one half but at a temperature higher than 900°C. it is

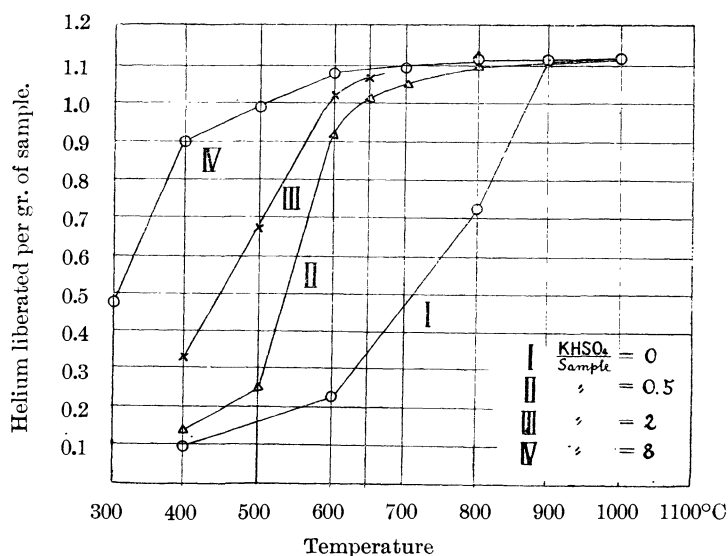


Fig. 3.

given off almost completely. The other curves (II, III & IV) show the quantities of helium evolved when the mineral is fused with KHSO_4 at various temperatures, each curve corresponding to each different amount of the fusing agent as noted in the figure. The more the fusing agent is used, the easier the helium in the mineral comes off at any temperature below 900°C . But at 1000°C . the gas in the mineral is liberated completely, independently of the amounts of the fusing agent.

TABLE 4.

Amount of fusing agent	Fusion temp. ($^\circ\text{C}$.)	Amount of mineral used (gr.)	Helium evolved (c.c.)	Helium per gr. of mineral (c.c.)
Mere heating without fusing agent	400	1.4992	0.144	0.096
	600	1.9984	0.472	0.236
	800	1.5011	1.099	0.732
	900	1.3512	1.499	1.109
	1000	1.9992	2.238	1.119
$\frac{\text{KHSO}_4}{\text{mineral}} = \frac{1}{2}$	200	1.0003	0	0
	400	1.0003	0.134	0.134
	500	1.0018	0.250	0.250
	600	1.0013	0.919	0.918
	650	1.0001	1.017	1.017
	700	1.0020	1.051	1.049
	800	1.0002	1.100	1.100
	1000	0.9993	1.121	1.122
$\frac{\text{KHSO}_4}{\text{mineral}} = 2$	400	1.0013	0.337	0.337
	500	1.0007	0.653	0.653
	600	1.0003	1.050	1.050
	650	1.0003	1.070	1.070
$\frac{\text{KHSO}_4}{\text{mineral}} = 8$	200	0.9995	0	0
	300	0.9997	0.480	0.480
	400	0.5004	0.448	0.897
	500	0.5018	0.494	0.984
	600	0.5010	0.542	1.082
	700	0.5003	0.548	1.095
	800	0.5005	0.565	1.129
	1000	0.4994	0.563	1.127

Helium in the Monazite⁽¹⁾ from Ishikawa. The result of experiments on the monazite is shown in Table 5. When the mineral is heated at

- (1) J. Sasaki determined the amount of helium which was liberated by this mineral on red heat, and assuming that the quantity was half the whole content of helium, he calculated the age of the mineral (this journal, 1 (1926), 253).

1000°C., it gives off nearly the whole of its helium within several hours, what is found to agree with the result of D.O. Wood's experiment.⁽¹⁾ The helium in the mineral is also liberated almost completely when it is heated with sulphuric acid at a lower temperature for a longer time. Table 6 and Fig. 4 give the temperature effect on the liberation of helium. Five hours' heating at 600°C. makes the sample to give off not more than half the helium present in the mineral, but at a temperature above 800°C. the whole of the gas is emitted for the time.

TABLE 5.

Amount of mineral used (gr.)	Method of treatment	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
4.9991	Heating at 800°C. for 5 hours.	1.115	0.223
3.1254	"	0.725	0.232
3.6709	Heating at 1000°C. for 5 hours.	0.903	0.246
9.9983	Heating at 320°C. with conc. H ₂ SO ₄ for 3 hours.	2.109	0.211

TABLE 6.

Amount of monazite used (gr.)	Heating temperature (°C.)	Heating duration (hours)	Helium evolved (c.c. at N.T.P.)	Helium per gr. of mineral (c.c.)
4.9970	400°	5	0.140	0.028
4.9953	600	"	0.734	0.147
3.1254	800	"	0.725	0.232
3.6709	1000	"	0.903	0.246

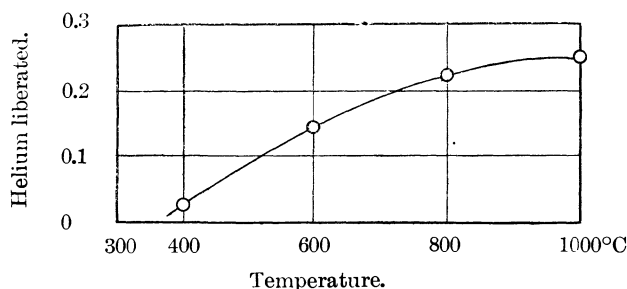


Fig. 4.

(1) *Proc. Roy. Soc. London*, A **84** (1911), 70.

Helium in the Samarskite and the Monazite from Ishikawa. For the liberation of helium in these two minerals, only the heating method is used for the deficiency of the samples. But as the minerals are heated at 1000°C., it may be reasonably acknowledged in view of the results obtained in the cases of ishikawaite and monazite, that each of the minerals loses the whole of its helium.

TABLE 7.

Kind of mineral	Amount used (gr.)	Method of treatment	Helium evolved (c.c.)	Helium per gr. of mineral (c.c.)
Samarskite	3.0011	Heating at 1000°C. for 3 hours.	4.263	1.420
Xenotime	3.2812	Heating at 1000°C. for 2 hours.	0.083	0.025

Calculation of the Ages of the Radioactive Minerals.

The age of a primary radioactive mineral can be calculated from its contents of uranium, thorium and one of their disintegration products, helium or lead. The contents of uranium and thorium in the ishikawaite have been determined by the method of Prof. Y. Shibata,⁽¹⁾ and the amount of lead in the same sample has been measured according to the analytical process outlined in the Table 8. The analysis gives the following result:

Uranium, 20.86% (23.65% as UO₂).

Thorium, nil.

Lead, 0.36%.

For the calculation of the ages of the samarskite and the monazite, the data of Profs. Y. Shibata and K. Kimura⁽²⁾ on the uranium and thorium contents of the minerals are used.

Samarskite: uranium, 14.87%; thorium, nil.

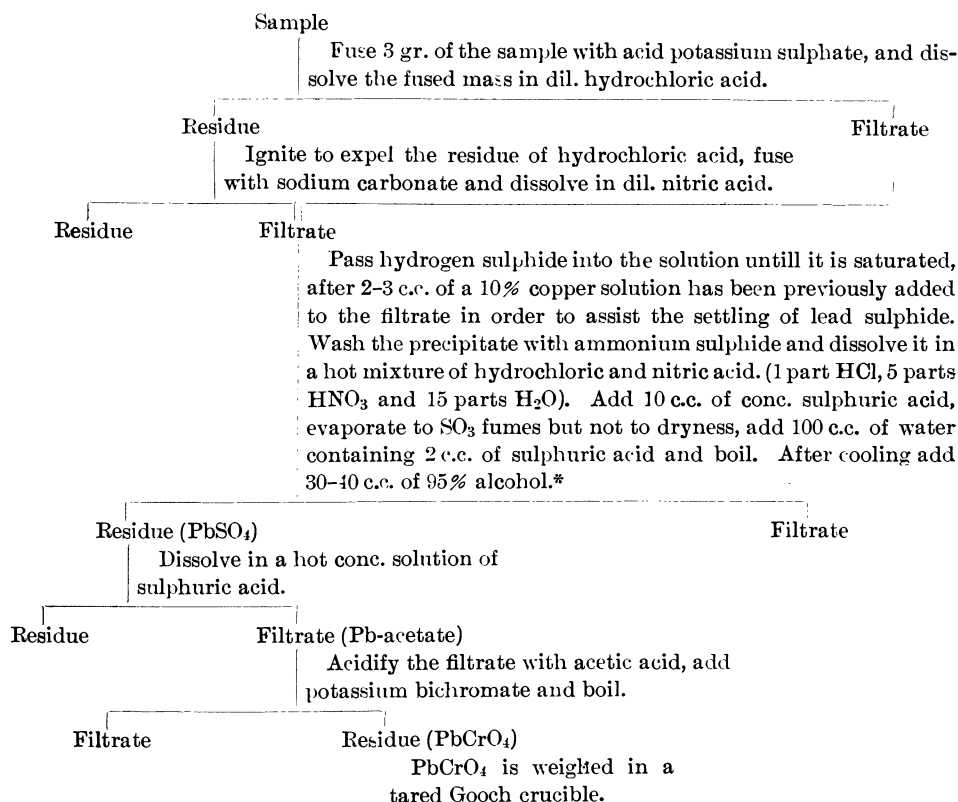
Monazite: uranium, 0.37%; thorium, 8.50%.

(1) *J. Chem. Soc. Japan*, **43** (1922) 307.

(2) *J. Chem. Soc. Japan*, **43** (1922) 301; **42** (1921), 961.

TABLE 8.

Method of the determination of lead in ishihawaite.



* see W. Scott, "Standard Method of Chemical Analysis". Vol. 1, p. 208.

If (*U*), (*Th*) and (*Pb*) denote the percentage contents in a mineral of uranium, thorium and lead of radioactive origin respectively, the age in millions of years of mineral is given approximately by the formula,

$$\text{Age} = \frac{(Pb)}{(U) + k(Th)} C,$$

where *k* and *C* are constants, the most trustworthy values of which have been given by A. Holmes and W. Lawson⁽¹⁾ to be: *k*=0.38 and *C*=7.400. The correction may be made for the wearing out of uranium and thorium during the life-time of the mineral, but it can be neglected in the case of relatively young minerals as those from Ishikawa.

(1) *Am. J. Science*, 76 (1927), 327.

Another expression for the age of a mineral by the helium method is given by A. Holmes and W. Lawson, thus

$$\text{Age} = \frac{(He)}{(U) + 0.29(Th)} \times 8.5 \text{ million years,}$$

where (U) and (Th) denote the percentage contents of the uranium and the thorium in the mineral respectively, and (He) , the volume in c.c. of helium at N.T.P. in 100 gr. of the mineral.

According to these formulas the ages of the minerals occurring in Ishikawa have been calculated from the data given in preceding pages.

$$\begin{aligned} \text{Age of the ishikawaite} &= \frac{(He)}{(U) + 0.29(Th)} \times 8.5 \\ &= \frac{177.5}{20.85} \times 8.5 = 72.3 \text{ million years} \\ &\quad \text{(by the helium method)} \\ &= \frac{(Pb)}{(U) + 0.38(Th)} \times 7,400 \\ &= \frac{0.36}{20.85} \times 7,400 = 127 \text{ million years} \\ &\quad \text{(by the lead method).} \end{aligned}$$

$$\text{Age of the samarskite} = \frac{142.1}{14.87} \times 8.5 = 81.2 \text{ million years.}$$

$$\text{Age of the monazite} = \frac{24.6}{0.37 + 0.29 \times 8.5} \times 8.5 = 73.9 \text{ million years.}$$

It is to be naturally expected that the age calculated with lead as an index is greater than the age calculated from the amount of helium present in the mineral. Such is shown in the case of the ishikawaite.⁽¹⁾

The result of calculation shows that these three minerals from Ishikawa belong to almost a same geological age which must be considered to be Jurassic or early Crataceous. This consideration is justified by the direct evidence that the pegmatites in which these minerals occur are regarded to belong to the Mesozoic Group.

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(1) Y. Uzumasa gives 29.2 million years as the age of the ishikawaite, determining the amount of lead in the mineral by a colorimetric method, but his value appears to be too small (see *J. Chem. Soc. Japan*, **48** (1927), 406).

ELECTRODE POTENTIAL OF NICKEL. PART II. EFFECT OF OCCLUDED HYDROGEN ON THE ELECTRODE POTENTIAL OF NICKEL.

By Kwanji MURATA.

Received September 15, 1928. Published October 28, 1928.

In the first paper⁽¹⁾ it was reported that the nickel electrodes which had been freshly prepared from finely powdered nickel oxide by being reduced in hydrogen, and which probably occluded hydrogen, gave an accurately reversible and reproducible electrode potential. But Schoch,⁽²⁾ and Richards and Behr⁽³⁾ reported that in their experiment the occluded hydrogen in nickel or iron gave an indefinite and abnormally lower potential. Their results are in conflict with those obtained by the present writer for a nickel electrode. The experiments described in this paper were therefore undertaken with the purpose of deciding whether such occluded hydrogen has actually any considerable effect on the potential or not.

According to Thiel and Hammerschmidt⁽⁴⁾ while ordinary nickel does not occlude much hydrogen when it is simply heated in the gas, (0.15 times its volume of hydrogen at 200°C, and 0.68 times at 800°C.), it can take up 11–18 volumes of hydrogen at room temperature under the stimulus of a prolonged cathodic polarization. These values perhaps are not to be taken as absolute but only show the relative absorbing power under varying conditions. Considerable differences have been reported by other observers; these being mainly due to the varying modes and temperatures of preparation and to the conditions of absorption to which it is subjected. Thus, according to Taylor and Burns⁽⁵⁾ who made a most thorough study of this subject, some powdered nickel which had been reduced from the oxide at various temperatures absorbed an amount varying from 0.2 to 5 of its volume of hydrogen, decreasing rapidly as the temperature rise. Sieverts⁽⁶⁾ has shown that nickel dissolves from 0.18 to 1 volume of hydrogen at the temperatures between 200° and 1000°C., the solubility increasing almost proportionally with increasing temperature, and also that the amount of hydrogen retained by nickel is proportional to the square root of the gaseous pressure.

(1) This journal, **3** (1928), 57.

(2) *Am. Chem. J.*, **41** (1909), 208.

(3) *Z. physik. Chem.*, **58** (1907), 301.

(4) *Z. anorg. allg. Chem.*, **132** (1924), 15.

(5) *J. Am. Chem. Soc.*, **43** (1921), 1277.

(6) *Z. physik. Chem.*, **77** (1911), 591.

Hence the gas absorbed will be given off when the partial pressure is smaller.

On the other hand, Raoult⁽¹⁾ reported that a very porous nickel when polarized cathodically can be made to absorb about 165 times its volume of hydrogen. The amount actually occluded depends on the strength of the current and on the physical nature of the nickel. This extraordinary occlusion of hydrogen is only temporary and the main part of the excess is gradually evolved as the current ceases but the rest of the hydrogen is very tenaciously retained by the nickel, forming a kind of solid solution, and can be removed from it only on heating under a reduced pressure. It is well known that electrolytically deposited nickel when heated under reduced pressure gives off hydrogen showing that it, too, occludes hydrogen.

Consequently the first experiment was undertaken in order to find the effect of the hydrogen, produced in nickel by cathodic polarization, on the potential of the nickel electrode.

The second series of experiments was carried out, in an atmosphere of nitrogen in order to determine the effect of the hydrogen occluded by the nickel during its reduction. However, there seemed to be no doubt that the nitrogen used by the present writer was not pure but contained a trace of oxygen owing to the great difficulty in its complete removal, and there is some ambiguity, therefore, in the results of these experiments.

For this reason, the third experiment was carried out in an atmosphere of nitrogen mixed with a little excess of hydrogen over the quantity required to remove the oxygen, with the purpose of deciding the point by comparing the effects of the various concentrations of hydrogen.

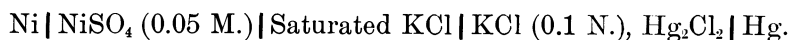
Apparatus and Method of Experiment. The electrode vessel and the apparatus for preparing the nickel half-cell were the same as those which served for the former experiments (see "Electrode potential of nickel. Part I," Fig. 1, this journal, 3 (1928), 59). When it was desired to polarize the nickel electrodes with hydrogen, the cell was filled with dilute sulphuric acid which had been stored in one of the reservoirs, H', and freed from air by passing hydrogen through it, as done in the case of the electrolyte in reservoir H. After the cell had been filled with the acid, as an anode against the nickel electrode a long platinum wire was inserted into the branch tube, f, by releasing the pinch-cock, Q, and through that tube a slow current of the acid solution was allowed to flow freely before and during the course of polarization, in order to prevent any possible diffusion of oxygen into the electrode chamber. After closing the cocks Q and k, the cell having been carefully washed was filled with nickel sulphate solution.

On the other hand, when it was required to work with nitrogen or nitro-

(1) *Compt. rend.*, 69 (1869), 826.

gen with hydrogen added, the cell, after the reduction was completed, was freed from hydrogen through i by an oil pump, the cocks Q and k being closed. The cell was allowed to stand under the reduced pressure for about half an hour and then filled with the gas. The pumping out and filling was repeated several times at 300°C. to remove any hydrogen which might have been occluded by the nickel electrode. In other respects, the procedure was nearly the same as was described in the former paper.

Results of Measurements of Electromotive Force. The combination of the cell was as follows :



In these experiments 0.05 mol NiSO_4 was always used and the measurements were made at 25°C. The current always flowed in the cell from left to right.

For the sake of comparison the results obtained in the three series of the experiments are summarised in Table 1. In Fig. 1 are plotted the changes with time of the electromotive forces of these cells.

TABLE 1.

E.M.F. of cell : $\text{Ni} | \text{NiSO}_4 (0.05 \text{ M.}) | \text{Sat. KCl} | \text{KCl} (0.1 \text{ N.}), \text{Hg}_2\text{Cl}_2 | \text{Hg}$, at 25°C.

Elapsed time in hours	E.M.F. in volt.				
	Cell No. 5	Cell No. 6	Cell No. 7	Cell No. 7'	Cell No. 8
1	-0.6348	-0.63105	-0.63240	-0.63660	-0.6388
2	-0.6350	-0.63125	-0.63275	-0.63660	-0.6388
4	-0.6353	-0.63130	-0.63345	-0.63655	-0.6387
7	—	—	-0.6338	-0.63655	—
12	—	—	—	—	—
17	-0.6355	-0.6326	-0.6345	—	-0.6385
24 (1 day)	-0.63565	-0.6332	-0.6346	-0.6368	-0.6384
36	-0.63575	-0.6335	-0.6351	-0.6369	-0.6382
48 (2 days)	-0.6359	-0.6337	-0.6354	-0.6370	-0.6380
					H ₂ on
60	-0.63600	-0.6339	-0.6355	-0.6372	-0.6379
72 (3 days)	-0.6361	-0.63405	-0.6355	-0.6373	-0.63785
84	—	-0.63415	-0.63545	-0.63725	-0.63780
					O ₂ on
85	—	—	—	—	-0.5692
96 (4 days)	-0.6361	-0.6343	-0.6354	—	-0.5868
108	—	-0.6344	-0.6354	—	—
120 (5 days)	-0.6360	-0.6344	-0.6353	-0.63705	—
				O ₂ on	
121	—	—	—	-0.5984	—
132	—	-0.6345	-0.6353	-0.6233	—
144 (6 days)	—	-0.6346	-0.6353	—	—
168 (7 days)	—	-0.63455	—	—	—
288 (12 days)	—	-0.6340	—	—	—
		O ₂ on			
289	—	-0.5612	—	—	—

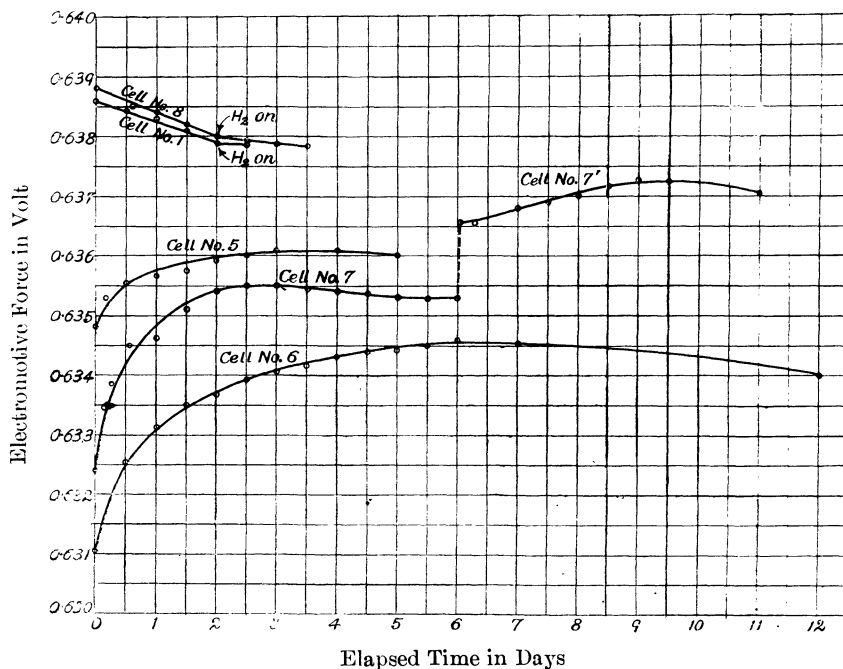


Fig. 1

(I) *Effect of the hydrogen produced in nickel by cathodic polarization.* The electrode material in cell No. 5 was prepared exactly in the same way as that in cell No. 1, and it was subjected to cathodic polarization in a decinormal solution of sulphuric acid for five hours with 30 milliamperes at 110 volts. Though the polarization was carefully carried out, the electromotive forces observed with four electrodes in the case of this cell were often found not to agree with each other to a closer precision than ± 0.0005 volt at the beginning of the measurement.

From the results in the case of cell No. 5, as compared with those of cell No. 1, it will be seen that a prolonged cathodic polarization in dilute acid does not cause any increase but rather a slight decrease of the electromotive force, this showing that the results are in conflict with those obtained by previous investigators; i.e. those in the case of the experiments of Schweitzer⁽¹⁾ with the polarized nickel electrode in caustic alkali solution, of Schoch⁽²⁾ and of others with the nickel polarized in dilute acid or in water, and with the similar experiments of Richards and Behr⁽³⁾ with iron, and of Schildbach⁽⁴⁾ with cobalt, all of which showed that the cathodic polarization

(1) *Z. Electrochem.*, **15** (1909), 607.

(2) *Loc. cit.*

(3) *Loc. cit.*

(4) *Z. Electrochem.*, **16** (1910), 967.

caused the increase in the electromotive forces. But, all these previous investigators worked under conditions in which there was the possibility that their electrodes might have come in contact with the air during the course of their preparation.

The initial value of the electromotive force in cell No. 5, contrary to expectation, showed a value about 4 millivolts smaller than that in cell No. 1; but this value increased with time to the extent of as much as a few millivolts. At present it is impossible to explain this diminution in the initial value of the electromotive force clearly, but it is supposed that it may be the effect of a trace of the free acid, which might have remained in the cell, owing to the difficulty of the replacing it,—it is impossible to avoid this trouble completely,—especially as the nickel was placed on the platinum wire in the cell as the electrode material, since nickel, which was reduced by the writer's method, evolves hydrogen instantaneously when it comes in contact with sulphuric acid, even when the acid is very dilute. According to the record of the subject, Schoch⁽¹⁾ in his experiments on the influence of free acid on the nickel-calomel cell found that even a trace of it caused a marked decrease in the electromotive force. A similar phenomenon was observed by the author in the investigation of an iron electrode (unpublished).

(II) *Measurements in an atmosphere of nitrogen.* The electrode materials in cell Nos. 6 and 7 were prepared in the same way as those in cell No. 1, and then the hydrogen was replaced by nitrogen. In the case of cell No. 6, nitrogen was passed through the electrode vessel for an hour with a speed of two or three bubbles per second (about 50 c.c. per minute) and no repetition was made, while in that of cell No. 7 the method was carried out in the same way as has already been stated. The electrolyte used in both cells was prepared from the same stock solution, and was given as nearly as possible the same treatment.

As the result, for the two cells curves of nearly the same type were obtained as shown in Fig. 1. The initial values of the electromotive forces in both cases were considerably less as compared with that of cell No. 1 and, increasing at first, rapidly arrived at their own maximum values and remained almost constant. There is, however, a considerable difference (1.4 mv.) between the initial values of the two cells, an amount which is too large to be neglected as an experimental error, because the agreement of the individual electrodes of each cell was excellent, and the mean deviation was within only 0.05 mv.

In the case of cell No. 7, after six hours of measurement, the entire solution was removed, the electrodes thoroughly washed, and the cell was refilled with a fresh solution which had been saturated with hydrogen. The result-

(1) Loc. cit.

ing value of the electromotive force measurements increased almost immediately to 0.6366 volt then gradually approached the value of cell No. 1, and finally in three days reached the maximum value of 0.6373 volt where it remained nearly constant. The results given in Fig. 1 are those of cell No. 7'.

The low initial electromotive force of cells Nos. 6 and 7 as compared with that of cell No. 1 may at first sight be attributed to the removal of the hydrogen which had been absorbed by the nickel in the course of reduction. But, such an explanation is inconsistent with the fact that cell No. 7, in which a more complete removal of hydrogen must have been accomplished by the repeated evacuation, did not show a greater lowering of the electromotive force than cell No. 6. This discrepancy led the writer to find the cause in an entirely different direction which is explained as follows.

The nitrogen used in these experiments was obtained by the fractional distillation of liquid air and contains 2-3% of oxygen. It was purified by being passed through three washers of alkaline solution of potassium permanganate, and then through a solid caustic alkali tube, was freed from oxygen by being passed through a combustion tube filled with copper, and was then dried by being passed through a solid caustic soda tube. But, it has been noticed by several workers⁽¹⁾ that by such an ordinary method as was used by the present writer a small amount of the oxygen in nitrogen cannot be completely removed from the nitrogen.

On the other hand, it has already been stated at the beginning of the first paper that even a trace of oxygen greatly affects the potential of nickel. It was actually observed by the writer himself that electromotive forces were almost immediately lowered more than 30 millivolts further by the introduction of a small amount of air after the above measurements had been made. Putting these facts together, it seems very proper to attribute the low electromotive forces in cells Nos. 6 and 7, as compared with cell No. 1, to the effect of the oxidation of nickel occurring during the passage of nitrogen. Then, the higher electromotive force of cell No. 6, as compared with that of cell No. 7, is very well accounted for by the fact that a much larger volume of nitrogen was used in the former and accordingly, a comparatively heavier oxidation took place in it than in the latter.

In the end, this experiment in an atmosphere of nitrogen did not conclusively clear up the effect of the hydrogen contained in nickel on the electrode potential of the metal.

As for the gradual rise of the electromotive force in both cells, a full discussion will be given in the next paper in connection with the mechanism of the reactivation of passive metal.

(1) For example, Kautsky and Thiele, *Z. anorg. allg. Chem.*, **152** (1926), 342.

In the second place, the sudden rise of the electromotive force in cell No. 7' will be discussed. A sudden rise of the electromotive force caused by the solution saturated with hydrogen in cell No. 7' seems to have a close connection with the lowering of the electromotive force above explained. Schoch⁽¹⁾ has also observed that in a cell of the same type but with $1N\cdot NiSO_4$ there is remarkable sudden rise in the electromotive force upon passing hydrogen through the cell, in which all the electrodes used were those which had been kept in air or those that have had a chance of coming in contact with the air. In his experiments the electromotive force was increased by 150 mv. by the passage of hydrogen, reached the abnormally high value of 0.337 volt, and then decreased gradually to the normal value—the electromotive force of the cell with $1N\cdot NiSO_4$ calculated from the electromotive force for a $0.1N\cdot NiSO_4$ solution measured by the present writer is 0.276 volt.

From these facts, as compared with the results in the case of cell No. 1 where no appreciable change occurred upon the passing of hydrogen, it seems that the introduction of hydrogen causes a marked change in the potential only when the electrode has been previously brought into superficial oxidation by exposure to the air or oxygen, and that the change depends on the degree to which it has been affected.

There is no doubt that the sudden rise in the electromotive force of cell No. 7' is due to the change on the very surface of the nickel which instantly takes place on its contact with the hydrogen dissolved in the solution. However it is not easy to understand how, under the conditions, such a sudden and remarked change can occur merely as the result of the physical adsorption of hydrogen by the nickel electrode.

Such a change must be considered to be very probably the result of the reduction of the oxide, once formed by the action of oxygen contained in the nitrogen. But the behaviour of hydrogen acting as an electrode must also be taken into account. The question as to which is the true cause of the sudden change above mentioned was answered by the next experiment which was made in an atmosphere of a mixture of nitrogen and hydrogen with the purpose of clearing up the nature of the effect of the hydrogen contained in nickel on the electrode potential of the metal.

(III) *Measurements in an atmosphere of nitrogen with the addition of hydrogen.* The experiment on cell No. 8 was carried out under the same conditions as in that of cell No. 7 with the exception of the atmosphere. The gas used in this experiment was prepared by mixing 9 volumes of N_2 and 1 volume of H_2 , which is a little over the quantity required to remove the oxygen contained in the nitrogen, and by passing the mixture through

(1) Loc. cit.

a heated palladised asbestos tube.⁽¹⁾ The electrodes were allowed to stand for about an hour at 300°C., a condition which is considered to be sufficient for the establishment of the equilibrium between the partial pressure of hydrogen in the gas phase and the hydrogen dissolved in the nickel.

At the beginning cell No. 8 gave an electromotive force of just the same high value and also the same type of change as that in cell No. 1 which was prepared in an atmosphere of hydrogen only. By this experiment, it was conclusively shown that the hydrogen dissolved in nickel has no effect on the electrode potential of nickel, because if there were any such effect, cell No. 8 should have given a value intermediate between those of cells Nos. 1 and 6.⁽²⁾

Secondly, if, as shown by Smits and Lobry du Bruyn⁽³⁾ the nickel electrode behaves as a hydrogen electrode in an atmosphere of hydrogen, as is the case with one of platinum, it is expected to produce a change of potential of nearly 0.08 volt, but as a matter of fact this result is not produced. Accordingly, it was confirmed that the sudden rise of the electromotive force of cell No. 7' by the introduction of hydrogen is due to the activation of the passive surface of the nickel. Further discussion of the mechanism of this activating action will be given in the next paper.

In short, as the result of the foregoing series of experiments the conclusion is reached that the hydrogen occluded by nickel has no effect upon the true electrode potential. For the measurement of the electrode potential of nickel, the complete exclusion of oxygen is the essential requirement and the use of the hydrogen atmosphere facilitates only the fulfillment of this requirement.

In conclusion, the writer wishes to express his great indebtedness to Professor G. Fuseya for his kind direction.

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- (1) The gaseous mixture was collected on water at 20°C. in a gas holder. Therefore, according to the writer's rough calculation the amount of hydrogen required to remove all the oxygen in the nitrogen and also that dissolved in water in the gas holder was found to be about 8% of the nitrogen. The quantity of oxygen dissolved in water was calculated from the solubility of air in water at 20°C. and the whole volume in the gas holder. No attempt was made to find the concentration of hydrogen remaining in the gas, but from the quantity of the oxygen in the nitrogen it was calculated that the concentration of hydrogen was not more than 5% at most.
 - (2) If the quantity of hydrogen absorbed by nickel is proportional to the square root of the hydrogen pressure, as reported by Sieverts (*loc. cit.*), the hydrogen content of the nickel in cell No. 8 must have been less than twenty two hundredths of that in cell No. 1, since the hydrogen content of the gas was less than 5%.
 - (3) Smits, "Die Theorie der Allotropie" (1921), p. 412; *Proc. Acad. Sci. Amsterdam*, **20** (1918) 394.

Summary.

1. A prolonged cathodic polarization of the nickel electrode in dilute acid and in an atmosphere of hydrogen did not cause any increase, but rather a slight decrease in the initial value of the electromotive force of the cell, $\text{Ni}|\text{SiSO}_4 (0.05 \text{ M.})|\text{KCl} (0.1 \text{ N.}), \text{Hg}_2\text{Cl}_2|\text{Hg}$. The effect of hydrogen produced in the metals of the iron group by cathodic polarization, i.e. of making the metals less noble as found by previous investigators, was not repeated in the case of reduced nickel powder. The slight diminution in the initial value of the electromotive force is supposed that it may be the effect of a trace of the free acid which might have remained in the cell, owing to the difficulty of the replacing it.

2. The potentials of the nickel electrode in an atmosphere of nitrogen, and of nitrogen mixed with a little hydrogen were measured. As a result of these series of experiments the conclusion is reached that the occluded hydrogen in nickel has no effect upon the true electrode potential. But, it was observed that in the case of an electrode which has been once affected by oxygen, the effect of hydrogen is very remarkable, and the electrode returns to its active state even at a low temperature.

3. For the measurement of the potential of nickel electrode, the complete exclusion of oxygen is the essential requirement.

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THE IDENTITY OF THE TWO POSSIBLE ISOMERIC METHYL
ETHYL β -METHYL- α , γ -DICYANOGLUTACONATES.

By Yoshiyuki URUSHIBARA.

Received September 22, 1928. Published October 28, 1928.

By the previous investigations⁽¹⁾ it was shown that the condensation of $C_2H_5OCH:CXY$ with $CHNaX'Y'$, and the condensation of $C_2H_5OCH:CX'Y'$ with $CHNaXY$, where X, X', Y, and Y' represent negative groups such as CN and $COOC_2H_5$, give the same product, while generally the two compounds corresponding to the following formulae can be expected:

- (I) $XYC=CH-CNax'Y'$,
(II) $X'Y'C=CH-CNaxY$.⁽²⁾

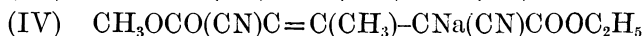
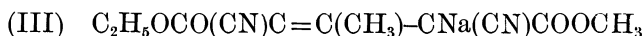
(1) This journal, **2** (1927), 278; **3** (1928), 219.

(2) Of course such arrangements of the negative groups that make the two formulae identical are out of the question.

Thus the sodium derivatives of the nitrile-esters of dicarboxy-glutaconic acid can not be obtained in two isomeric forms that differ from each other only in the positions of the double union and the sodium atom, but only one of the two is obtainable. It was already studied which of the two possible formulae must be assigned to the actually obtained substance in individual cases.⁽¹⁾

In order to make clear the mechanism of the condensations of this kind, it was important to know whether the products would prove also to be identical when two isomeric derivatives of β -methyl-dicarboxy-glutaconic acid which differ from each other only in the positions of the double union and the sodium atom were to be formed.

The author previously succeeded in the synthesis of diethyl β -methyl- α , γ -dicyanoglutaconate $C_2H_5OCO(CN)C:C(CH_3) \cdot CH(CN)COOC_2H_5$.⁽²⁾ This synthetical method was utilized for the preparation of the two possible isomeric methyl ethyl β -methyl- α , γ -dicyanoglutaconates. The condensation of ethyl ethoxy-ethylidene-cyanoacetate (α -cyano- β -ethoxy-crotonate) and methyl cyanoacetate in the presence of sodium methylate must yield the compound with formula (III), while methyl ethoxy-ethylidene-cyanoacetate and ethyl cyanoacetate must produce the compound with formula (IV) in the presence of sodium ethylate.



But the experiments showed that the products were the same, and this fact was already cited in a previous paper.⁽³⁾ The experimental data are given in the following pages.

The sodium compounds formed in the above condensations did not tend to crystallise, while the sodium derivative of the corresponding diethyl compound easily crystallised. Only the silver derivatives, which were obtained by double decomposition of the sodium compounds with silver nitrate in the aqueous solution, crystallised in colourless silky needles from hot alcoholic solution. In order to obtain any of the other metallic derivatives in crystalline form, the experiments on double decomposition of the silver compound with potassium, lithium, barium, and mercuric chlorides were tried without success. On concentrating the aqueous solutions none of the compounds of these metals was brought to crystallisation. It was anticipated that the free compounds, methyl ethyl β -methyl- α , γ -dicyanoglutaconates, which might be obtained from the sodium compounds, would be

(1) This journal, 3 (1928), 221.

(2) This journal, 3 (1928), 102.

(3) This journal, 3 (1928), 224.

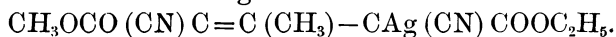
too easily changeable to be subjected to the processes of identification, for diethyl β -methyl- α , γ -dicyanoglutaconate itself had been found not to be obtainable in a stable form. Thus the author was obliged to compare the properties of the crystals of the silver compounds.

In the experiment of the refractive indices the silver derivatives of the diethyl compound previously prepared, and of the dimethyl compound newly synthesized were studied side by side with the methyl ethyl compounds.

Preparation. Ethyl ethoxy-ethylidene-cyanoacetate $C_2H_5OC(CH_3):C(CN)COOC_2H_5$ was added to the mixture of methyl cyanoacetate and the methyl alcoholic solution of sodium methylate, the quantities of the three substances being in the molecular proportion. The clear yellow solution was evaporated in vacuo over sulphuric acid to a viscous mass, and it was dissolved in water and the theoretical amount of silver nitrate (in aqueous solution) was added. The silver compound was precipitated in white voluminous powder, which was collected, washed with water, and dried in a desiccator. This silver compound was dissolved in hot absolute alcohol, which was filtered while hot and allowed to crystallise. The recrystallisation was repeated several times. A long boiling in alcoholic solution caused a change of the substance, producing insoluble crystals. Therefore a long heating was avoided in the recrystallisation. The silver compound obtained in this way was long silky needles. It was finely pulverised, dried in a desiccator and analysed. 0.2851 Gr. of the substance gave 20.85 c.c. of nitrogen at 23.5° , 752.8 mm.; 0.2595 gr. of the substance gave 0.3618 gr. of CO_2 and 0.0759 gr. of H_2O . (Found: N=8.10; C=38.03; H=3.27. $C_{11}H_{11}O_4N_2Ag$ requires N=8.16; C=38.48; H=3.23%.) (Specimen A) Considered from the mode of condensation this silver compound must have the following constitution:



By starting from methyl ethoxy-ethylidene-cyanoacetate, ethyl cyanoacetate, and an ethyl alcoholic solution of sodium ethylate, and pursuing the same experimental procedure, another specimen with the same composition was obtained. 0.3252 Gr. of the substance gave 23.75 c.c. of nitrogen at 22.5° , 756.4 mm.; 0.3058 gr. of the substance gave 0.4292 gr. of CO_2 and 0.0903 gr. of H_2O . (Found: N=8.14; C=38.29; H=3.30. $C_{11}H_{11}O_4N_2Ag$ requires N=8.16; C=38.48; H=3.32%.) (Specimen B) This compound must have the following constitution:

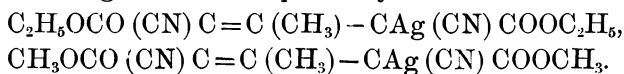


Methyl ethoxy-ethylidene-cyanoacetate had not been known, and was synthesised by the action of ethyl iodide on the silver derivative of methyl acetyl-cyanoacetate. It melts at $76-77^\circ$, nearly the same temperature at which the ethyl ester melts.

Equal parts of the specimens A and B were dissolved together in hot absolute alcohol and the solution was cooled. Thus the mixed crystals were obtained. (Specimen C).

The sodium derivative of dimethyl β -methyl- α , γ -dicyanoglutaconate was obtained by the condensation of methyl ethoxy-ethylidene-cyanoacetate with methyl sodio-cyanoacetate. On concentrating the methyl alcoholic solution the product crystallised gradually. The crystalline mass was dissolved in water and transformed into the silver derivative by double decomposition with silver nitrate. It was recrystallised from absolute alcohol. 0.3204 Gr. of the substance gave 24.2 c.c. of nitrogen at 22°, 758.2 mm.; 0.3140 gr. of the substance gave 0.4153 gr. of CO₂ and 0.0762 gr. of H₂O. (Found: N = 8.49; C = 36.08; H = 2.72. C₁₀H₉O₄N₂Ag requires N = 8.51; C = 36.47; H = 2.76%.)

The preparation of the diethyl compound was already described in the previous paper.⁽¹⁾ The diethyl and dimethyl compounds are represented by the following formulae respectively:



Identification. Photographs of X-ray spectra of the specimens A and B were taken by Debye-Scherrer's method. The lines on the two films coincided entirely. The K α -line of molybdenum was used. The most intense line corresponded to the lattice distance 3.56 Å. This line can not be attributed to metallic silver which might be produced by the decomposition of the substance on exposure to X-rays, for the lattice distance of the metallic silver is 4.06 Å.

The second method of identification was the comparison of the refractive indices. The crystals of all the three specimens A, B, and C gave the same results. They elongate in the direction of the optical elasticity axis X. Therefore n_1 (refractive index for the faster wave) is equal to α and constant around the zone of elongation. $\alpha_D^{27^\circ}$ was determined to be 1.503 ± 0.001 by the immersion method, and the character of zone was found negative.

The crystals of the dimethyl compound elongate also in the direction of the optical elasticity axis X; n_1 is equal to α , and constant around the zone of elongation. $\alpha_D^{27^\circ} = 1.518 \pm 0.002$. The character of zone is negative.

The crystals of the diethyl compound elongate in the direction of the optical elasticity axis Z; the character of zone is positive; and $\alpha_D^{27^\circ}$ was found to be nearly 1.580.

No difference has been found between the specimens A, B and C, and this fact reasonably leads to the conclusion that the specimen A, the con-

(1) This journal, 3 (1928), 104.

condensation product of ethyl ethoxy-ethylidene-cyanoacetate with methyl cyanoacetate in the presence of sodium methylate, and the specimen B, the condensation product of methyl ethoxy-ethylidene-cyanoacetate with ethyl cyanoacetate in the presence of sodium ethylate, are identical.

Although it is not yet able to decide whether the constitution of the condensation product is the type (III) or (IV), the condensations can be explained similarly as in the cases of the condensations of ethoxy-methylene compounds with sodio-methylene compounds, the fact that the methyl group in the β -position caused no peculiarity in the condensations being very favorable to this explanation.⁽¹⁾

The author is much indebted to Dr. I. Okada for photographing the X-ray spectra and measuring the refractive indices.

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(1) See this journal, 3 (1928), 223.

ELECTRODE POTENTIAL OF NICKEL.
PART III. MECHANISM OF THE RE-ACTIVATION OF
THE PASSIVE STATE OF NICKEL.

By Kwanji MURATA.

Received September 15, 1928. Published November 28, 1928.

In the former papers⁽¹⁾ only the experimental parts of the measurement of the electrode potential were described, while in the present paper the foregoing results are discussed from a thermodynamical standpoint and further the mechanism underlying the re-activation of the passive state of nickel is explained.

(I) **Catalytic Action of Nickel.** In Parts I and II, it has been shown that, if we exclude all traces of air or oxygen from the cell, the nickel gives a constant and reversible potential of active nickel in an atmosphere of hydrogen, and also of nitrogen; and that, if however the nickel used is one which has been affected by previous exposure to the air, the introduction of hydrogen causes rapid re-activation. The passive state of nickel, therefore, is extremely sensitive to hydrogen, and it is highly probable that the re-activation by hydrogen is a simple reduction of the surface of the superficially oxidized electrode. On the other hand, it has been definitely ascertained that nickel catalyses the combination of hydrogen and oxygen, an action which has a close relation to the above facts. Pease and Taylor⁽²⁾ have suggested that nickel will catalyse this reduction of the oxide even at room temperature. The work of Larson and Smith⁽³⁾ on the measurement of the synthesis of water in the presence of a nickel catalyst has shown that in the case of gas mixtures containing as much as 2% of oxygen the combination of hydrogen and oxygen occurs in contact with metallic nickel—even at low temperatures which are not far from room temperature—and this combination is fairly measurable at 34°C., though at these low temperatures a superficial oxidation of nickel readily takes place. They have also shown that the resulting nickel oxide is completely reduced at 34°C. in the presence of pure hydrogen. The same experimental results were repeated qualitatively by Benton and Emmett.⁽⁴⁾ According to the view of the two latter investigators, the

(1) This journal, 3 (1928), 57 and 253.

(2) *J. Am. Chem. Soc.*, 44 (1922), 1644.

(3) *J. Am. Chem. Soc.*, 47 (1925), 346.

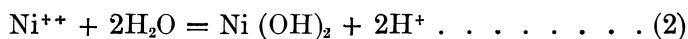
(4) *J. Am. Chem. Soc.*, 48 (1926), 632.

catalytic combination proceeds by a mechanism of successive oxidation and reduction, as found by Pease and Taylor⁽¹⁾ in their experiments on metallic copper. By the measurement of the rate of reduction of nickel oxide they have found that the reduction of this oxide by hydrogen is an interfacial reaction, proceeding at the interface between nickel oxide and nickel, that is, that there is a reaction the rate of which depends on the extent of the area and on the nature of the contact between the two solid phases. Consequently, starting with pure nickel oxide the initial rate is practically zero, but after a certain lapse of time, which is longer at lower temperatures, reduction begins and is accelerated autocatalytically.

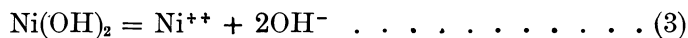
In view of these facts, it is reasonable to consider that the cause of the sudden change in nickel caused by the action of hydrogen from the passive state to the more active upon the introduction of hydrogen into the cell,—as found in cell No. 7' of the present writer's experiment or in the cell of Schoch⁽²⁾, the electrodes of which had been so affected by previous exposure to the air,—is mainly the catalytic reduction of the superficially oxidized surface of the nickel electrode.

The same catalytic action should have prevailed also in cells Nos. 6 and 7. However, for the fuller explanation of the results in the case of these cells, a theoretical calculation of the equilibrium conditions in the nickel half-cells is necessary, and this will be given in the next section.

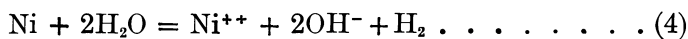
(II) **Nickel-Hydrogen Equilibrium in Aqueous Nickel Salt Solution.** In the nickel half-cell, there should be established an equilibrium between the electrode nickel and the hydrogen ion resulting from the hydrolysis of nickel salt, and the reactions involved will be expressed by the following equations:—



Combining these two with the equation for the dissociation of nickel hydroxide,



we have



Let K_1 , K_2 , K_3 , K_4 be the corresponding equilibrium constant of the reactions, respectively. Then, we have the relation,

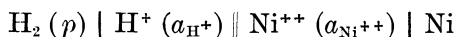
$$K_4 = K_1 \times K_2 \times K_3 = K_1 \times K_w^2 = p_{\text{H}_2} \times a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 \dots \dots \dots (5),$$

(1) Loc. cit.

(2) *Am. Chem. J.*, 41 (1909), 208.

where K_w is the dissociation constant of water. Therefore K_4 is obtainable, if K_1 is known.

Reaction (1) takes place in the cell,



The free energy decrease ($-\Delta F$) accompanying the change in state in this cell, and corresponding to the passage of two faradays, may be expressed by the following thermodynamic expression,

$$-\Delta F = 2FE_0 - RT \ln \frac{a_{\text{Ni}^{++}} \cdot p_{\text{H}_2}}{a_{\text{OH}^-}^2}$$

where E_0 is the normal electrode potential of nickel. The value of E_0 is -0.2496 volt at 25°C . according to the present writer's measurement. Therefore,

$$-\Delta F_{298} = 11518 - 1365 \log \frac{a_{\text{Ni}^{++}} \cdot p_{\text{H}_2}}{a_{\text{H}^+}^2}$$

At equilibrium, that is when $-\Delta F = 0$, we obtain

$$K_1 = \frac{a_{\text{Ni}^{++}} \times p_{\text{H}_2}}{a_{\text{H}^+}^2} = 10^{8.4387} \dots \dots \dots (6)$$

Taking $K_w = 1.005 \times 10^{-14}$ at 25°C .⁽¹⁾ from (5), we find that

$$K_4 = K_1 \times K_w^2 = 10^{-19.557}$$

$$p_{\text{H}_2} \times a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 = 10^{-19.557} \dots \dots \dots (7)$$

In this system the value of the product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ at equilibrium varies inversely with the variation of the partial pressure of the hydrogen, p_{H_2} . If the system is subjected to a definite pressure of hydrogen, the activity product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ will be fixed. Then when the partial pressure of the hydrogen is equal, for instance, to one atmosphere, equilibrium is attained at the point where the activity product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]$ equals $10^{-19.557}$. In an actual case, however, equilibrium can be established only when the value of the activity product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ in the solution at the equilibrium is less than or equal to that of the solubility product of $\text{Ni}(\text{OH})_2$. But, if the amount of this product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ be greater than that of the solubility product, the true equilibrium, being disturbed by the precipitation of nickel hydroxide, will not result.

Only a small amount of the work connected with the solubility product of $\text{Ni}(\text{OH})_2$ has been published and Britton's data⁽²⁾ are the only ones which

(1) Lewis and Randall, "Thermodynamics."

(2) *J. Chem. Soc.*, **127** (1925), 2118.

were obtained by direct measurement. By an electromotive force method he measured the H^+ concentration in the solution of nickel chloride with a sufficient amount of NaOH solution added to induce the precipitation of $Ni(OH)_2$. It is, however, doubtful whether this method gives the actual value of a_{H^+} , because the precipitate of nickel hydroxide in contact with the platinized-platinum should be continuously reduced by hydrogen, and the nickel thus produced would disturb its action as a reversible hydrogen electrode.

Therefore, the solubility product may be calculated indirectly by combining the hydrolysis constant of nickel sulphate and the solubility of nickel hydroxide in water.

Inserting Denham's value⁽¹⁾ of hydrolysis constant in equation (5), $K_2 = 1.1 \times 10^{-13}$ or $10^{-12.96}$, a value which is somewhat uncertain but the only one existing, we obtain the value of the ionization constant of nickel hydroxide,

$$K_3 = \frac{a_{Ni} \times a_{OH^-}^2}{a_{Ni(OH)_2}} = \frac{K_w^2}{K_2} \\ = \frac{(1.005 \times 10^{-14})^2}{1.1 \times 10^{-13}} = 10^{-15.04} \dots (8)$$

By the combination of this ionization constant with the solubility of nickel hydroxide in water,⁽²⁾ 1.27 mg./L. or 1.37×10^{-4} M/L., the molal concentration of nickel ion in the saturated aqueous solution of nickel hydroxide is found to be 3.16×10^{-7} or $10^{-6.50}$, from which, we have the solubility product,

$$[a_{Ni^{++}} \times a_{OH^-}^2]_{s.p.} = 1.256 \times 10^{-19} \text{ or } 10^{-18.91} \dots (9)$$

Solving equation (7) with this value of the solubility product, we have the corresponding partial pressure ${}_o p_{H_2}$,

$$\log {}_o p_{H_2} = -19.557 - 18.90094 = -0.657 \text{ or } \bar{1}.343 \\ {}_o p_{H_2} = 0.22 \text{ atm.} \dots (10)$$

This is the critical pressure, above which only equilibrium conditions can be attained and if the partial pressure of hydrogen is less than this value, the nickel will tend to go into solution accompanied by the precipitation of $Ni(OH)_2$ until p_{H_2} rises to the critical value. Hence, if p_{H_2} be greater than ${}_o p_{H_2}$, equilibrium will be always set up, but if the p_{H_2} be less than ${}_o p_{H_2}$, true equilibrium can never be attained and the nickel should continue to be attacked.

(1) *J. Chem. Soc.*, **93** (1908), 60.

(2) Almkvist, *Z. anorg. allg. Chem.*, **103** (1918), 240.

(III) **Discussion of the Results.** Now, the experimental results obtained in the former papers will be discussed in the light of the preceding theoretical considerations.

In the first place, the case of cell No. 1 will be considered, where a solution of 0.05 M. NiSO_4 (containing $a_{\text{Ni}^{++}} = 0.05 \times 0.24$) was in contact with the reduced nickel under one atmospheric pressure of hydrogen, and the pressure required for the system to be in equilibrium will be calculated. The hydrogen ion concentration in 0.05 M. NiSO_4 at 25°C . is found to be 3.95×10^{-5} or $10^{-4.40}$ by the graphic interpolation from Denham's values, though they are of less order of accuracy. Then, from equation (6),

$$p_{\text{H}_2} = \frac{K_1 \times a_{\text{H}^+}^2}{a_{\text{Ni}^{++}}} = \frac{10^{8.44} \times 10^{2 \times (-4.40)}}{0.05 \times 0.24} = 35.7 \text{ atms.}$$

The above calculation indicates that the nickel electrode is theoretically less noble than hydrogen under the conditions of the experiment and it should tend to go into solution with the evolution of the hydrogen on the nickel under one atmospheric pressure of hydrogen; the driving force for the corroding reaction is however

$$E_{\text{H}_2} = -\frac{RT}{2F} \ln p_{\text{H}_2} = 0.02958 \log 35.7 = 0.0459 \text{ volt at } 25^\circ\text{C}.$$

It is owing to this relatively small difference in the potential that the evolution of hydrogen is invisible, because the hydrogen overvoltage of nickel is usually high enough to offset the potential difference and prevent the gas evolution in bubbles. According to Thiel and Hammerschmidt,⁽¹⁾ the hydrogen overvoltage of nickel is 0.1375 volt.

On the other hand, in an atmosphere of nitrogen, as in cell No. 6 and No. 7, the nickel should go into the solution and form hydrogen until the solubility product of nickel hydroxide is attained; the oxidized surface of the passive nickel electrode will be reduced by the catalysis of nickel or destroyed, so that the nickel becomes gradually active. But, at the moment when the solubility product of nickelous hydroxide is reached, the value p_{H_2} in the electrode should be equal to p_{H_2} and no further solution of nickel can, therefore, take place. These are the reasons why the electromotive force of cells Nos. 6 and 7 rose gradually in the first, and then remained nearly constant at their own maximum values, i. e. above 0.6345 volt and 0.6355 volt, respectively, these values being a little below that of the active nickel in cell No. 1.

(IV) **Results of Previous Workers.** Now, with the above deduction, it seems possible to explain fairly the abnormal passive phenomena observed

(1) *Z. anorg. allg. Chem.*, **132** (1924), 15.

by previous workers in the measurements of the electrode potential of nickel.

In the first place, it is a remarkable fact that the potential of the nickel electrode is changed to an extraordinary degree on being treated with a solution of alkali hydroxide. The reversible potential of the reduced nickel in 1 N. NiSO_4 calculated from the writer's observed value is -0.276 volt, while in the case of the cathodic polarization of the electrode in an alkali solution a much less noble potential, i. e. as much as -0.33 volt, was found by Schweitzer⁽¹⁾; the latter potential, however, gradually changed appreciably. Another interesting experiment giving a very low potential, -0.597 volt was made by Muthmann and Fraunberger.⁽²⁾ The nickel having this low potential was prepared by electrolytic deposition on platinum from a neutral sulphate solution under a certain condition (at room temperature with 8 volts), and by the cathodic polarization of it with hydrogen in distilled water. Their experiment was however examined later by Thompson and Sage⁽³⁾ who found that the high potential observed by the former investigators was that of a green deposit of a basic salt and not one of pure nickel.

In this connection, it may be supposed as the most possible case that a thin muddy coating of some basic salt or a film of colloidal hydroxide precipitate is formed on the electrode by the previous treatment and that this coating or film is catalytically reduced by hydrogen into nickel in a very fine state. Since the lower the electrode potential, the finer the metal powder, it is natural that the extremely fine nickel powder should give such abnormally low potentials as those above mentioned at the moment, but that as this powder would tend to change to a more stable form with time the potential would gradually become normal.

If this is the case, then it is also possible that a similar abnormality may occur when the electrode is polarized even in an acid solution with hydrogen cathodically, so long as it has a chance of producing some basic salt or hydroxide on the very surface of the activated metal. This may possibly be the case when the activated surface, after being washed, has been wetted with water which might or might not contain the trace of acid, and was acted by the air while it was being transferred into the cell, as was done by Schoch.⁽⁴⁾

It will be remembered in this connection that pure iron quenched from an atmosphere of pure nitrogen gave a similar abnormality in its electromo-

(1) *Z. Elektrochem.*, **15** (1909), 607.

(2) *Sitz. Bayer. Akad. Wiss.*, **34** (1904), 201.

(3) *J. Am. Chem. Soc.*, **30** (1908), 714.

(4) Loc. cit.

tive force, as shown by the experiment of Richards and Behr.⁽¹⁾ This matter will be discussed in a paper which will be presented in the near future.

(V) **Free Energy.** The calculation of some important thermodynamic quantities relating to this subject have been made by combining the results obtained above with the existing data.

The Free Energy of the Formation of Nickel Hydroxide. Taking the solubility product of $\text{Ni}(\text{OH})_2$ as $10^{-18.90}$ the free energy change for the equation

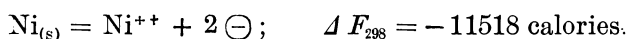


may be calculated

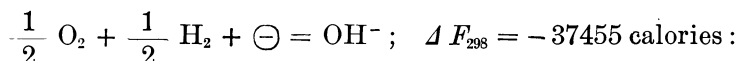
$$\Delta F_{298} = -RT \ln a_{\text{Ni}^{++}} \cdot a_{\text{OH}^{-}}^2 = -1365 \times -18.90 = 25800 \text{ calories.}$$

Then, the free energy of formation of $\text{Ni}(\text{OH})_2$ may be calculated as follows:—

From the first paper



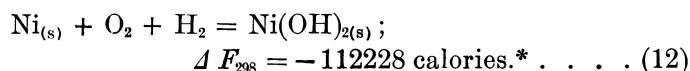
and, according to Lewis and Randall ("Thermodynamics"),



hence

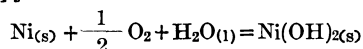


Combining this value with that of (11) determined above, we have for the standard free energy of formation of $\text{Ni}(\text{OH})_{2(s)}$,

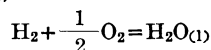


(1) *Z. physik. Chem.*, **58** (1907), 301.

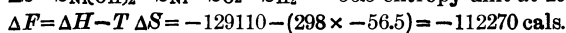
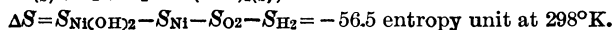
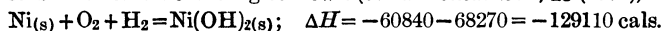
* The value obtained from the solubility product used in the present paper is in good agreement with that obtained from the heat of formation of $\text{Ni}(\text{OH})_2$ using the Nernst heat theorem, the entropy of the elements (Lewis and Randall, "Thermodynamics" p. 464) at 25°C. and the formula proposed by Latimer (*J. Am. Chem. Soc.*, **43** (1921), 818) for the entropy of solid salt. The heat of formation of $\text{Ni}(\text{OH})_2$ in the reaction,



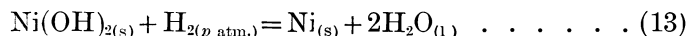
is 60840 cal. according to Thomsen (Landolt-Börnstein, "Physikalisch-Chemische Tabellen"), and that of the reaction



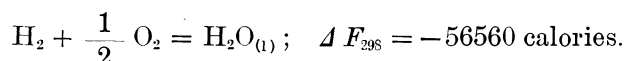
at 25°C. is 68270 cal. according to Lewis (*J. Am. Chem. Soc.*, **28** (1906), 1390), hence for



The Free Energy Change in the Reduction of Nickel Oxide or Nickel Hydroxide. The free energy change in the reaction,



may be obtained from (12) by combination with the free energy of the formation of water. According to Lewis and Randall,⁽¹⁾



hence

$$\Delta F_{298} = 112,228 + 2 \times (-56560) - 1365 \log p_{\text{H}_2}^*$$

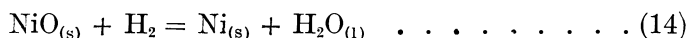
When $p_{\text{H}_2} = 1 \text{ atm.}$, then $\Delta F_{298} = -892 \text{ calories.}$

Therefore, the driving force of this reaction is

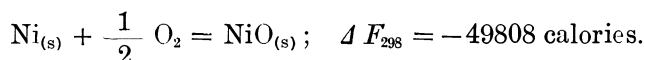
$$E = \frac{892}{2 \times 23074} = 0.0193 \text{ volt.}$$

Even at 25°C. there is a small driving force tending to reduce $\text{Ni}(\text{OH})_2$ to Ni, forming water. This accounts for the fact that the spontaneous reduction of nickelous hydroxide takes place under one atmospheric pressure of hydrogen, especially when it is in contact with a catalyst, such as a platinized platinum or nickel.

The free energy change for the reaction,

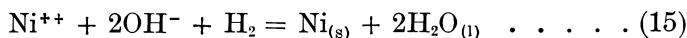


may be obtained using the value of the free energy of formation of NiO. The present writer calculated the free energy of formation of NiO from the experimental data of Pease and Cook,⁽²⁾ and found it to be 49808 calories, while the value reported in Pease and Cook's paper is 56497 calories.



therefore $\Delta F_{298} = 49808 - 56560 = -6752 \text{ calories.}$

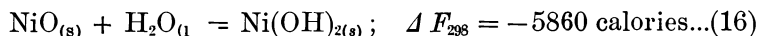
And the free energy for the reaction



may be calculated from (7)

$$\Delta F_{298} = -1365 \times 19.557 = -26695 \text{ calories.}$$

Therefore combining reaction (14) and (15), we obtain

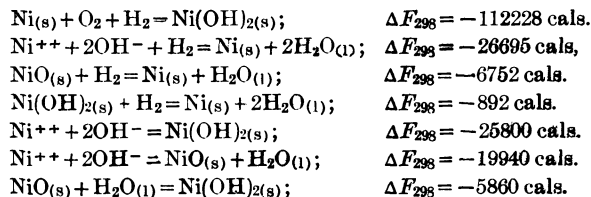


(1) Loc. cit.

(2) *J. Am. Chem. Soc.*, **48** (1926), 1196.

* The value of p_{H_2} which is the critical partial pressure at equilibrium may also be obtained from this equation by putting ΔF equal to zero.

The results above obtained are summarized as follows for the sake of comparison.⁽¹⁾



The writer wishes to express his great indebtedness to Professor G. Fuseya for his kind direction.

Summary.

1. The re-activation by the action of the hydrogen of the nickel electrode, which has once been affected by oxygen, has been explained on the ground that nickel itself behaves as a catalyser, on the combination of oxygen and hydrogen.

2. It has been thermodynamically deduced that the equilibrium conditions in the nickel half-cells are expressed by $p_{\text{H}_2} \times a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 = 10^{-19.66}$, from which it has been calculated that when the activity-product ($a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2$) attains the solubility product of nickel hydroxide, the corresponding partial pressure of hydrogen is 0.22 atm. This is the critical pressure above which only equilibrium can be established and if the partial pressure of hydrogen is less than this value the nickel will tend to go into solution accompanied

- (1) The writer calculated the solubility product of $\text{Ni}(\text{OH})_2$ also from the experimental data of Britton (*J. Chem. Soc.*, 127 (1925), 2114) by the following method and found it to be 2.0927×10^{-17} , while the value reported in Britton's paper is 8.7×10^{-19} . This was done by taking into consideration the decrease in nickel ion concentration resulting from the addition of 0.8 c.c. of 0.0967 N. NaOH to 100 c.c. of 0.025 M. NiCl_2 to produce incipient precipitation, by obtaining the activity of Ni^{++} in the solution, taking 0.38 as the activity coefficient at that concentration (Lewis and Randall, "Thermodynamics" p. 382), and combining this activity with the observed value of $a_{\text{OH}^-} = 10^{-7.33}$ in the resulting solution.

$$a_{\text{Ni}^{++}} = 0.38 \times \left(2.5 \times 10^{-2} - \frac{0.0967 \times 0.8}{2 \times 100} \right) = 0.00935$$

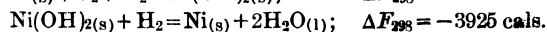
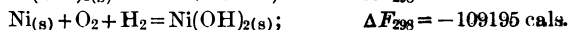
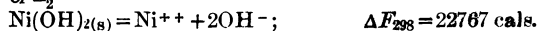
$$a_{\text{OH}^-} = 10^{-7.33}$$

hence,

$$a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 = 0.00935 \times 10^{-2 \times 7.33} = 2.0927 \times 10^{-17} \text{ or } 10^{-16.68}$$

This value being adopted the values of p_{H_2} and the free energies of the following reactions become,

$$p_{\text{H}_2} = 0.0013 \text{ atm.}$$



by the precipitation of nickel hydroxide until p_{H_2} rises to the critical pressure.

3. On the above deduction, the changes with time in the electromotive force of the cells which were prepared in the atmosphere of hydrogen or of nitrogen have been explained.

4. The abnormal behaviour of the nickel electrode observed by previous investigators has also been discussed on the same basis of proof.

5. The changes in free energy of various reactions have been calculated.

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THE PREPARATION OF TRIACETYL STARCH AND ITS MOLECULAR WEIGHT.

By Yojiro TSUZUKI.

Received October 4, 1928, Published November 28, 1928.

Although it is quite necessary, in the study of starch, to get the solution of starch or of its derivatives, yet our knowledge of this field is far from being complete. The author has given a convenient method of preparing acetyl derivative of starch yielding a large quantity of it at a time, has examined its solubility in various solvents, and has estimated its molecular weight in several media by the cryoscopic and the ebullioscopic methods.

The Acetylation of Starch.

Acetylation of starch has already been carried out in various ways,⁽¹⁾ among which there are fairly available methods such as that with acetic anhydride and pyridine⁽²⁾ and that with acetic anhydride and sulphuric acid,⁽³⁾ but still they either take a long time (a few days or more) or are apt to give more or less depolymerised products. It is readily understood that starch cannot be expected to undergo mild acetylation without difficulty in the absence of suitable dispersing medium either for the starch or for the reaction product as in the case of the usual acetylating methods.

(1) See M. Samec, "Kolloidchemie der Stärke," (1927), p. 436.

(2) M. Bergmann and E. Knehe, *Ann.*, **452** (1927), 141.

(3) F. Pregl. *Monatsh.* **22** (1901), 1049; H. Pringsheim and K. Wolfsohn, *Ber.*, **57** (1924), 887..

The author has succeeded in preparing acetyl starch quite easily, overcoming the above difficulty in the following way :

Fourty grams of starch⁽¹⁾ (air-dry, containing 7% of water) are mixed up with a saturated aqueous solution of zinc chloride (50 gr. of anhydrous salt in 23 gr. of water) to a *transparent sticky paste*, heating on the water bath, and 220 c.c. of acetic anhydride are gradually added, a part of which is at first converted by the water into acetic acid, which plays an important rôle as a nice solvent for the acetyl starch which is to be produced. As water often acts with acetic anhydride violently the reaction mixture is carefully warmed (sometimes it must be cooled) with constant stirring on the water bath, the temperature not far exceeding 70°. After the water is acted the gelatinized starch goes into solution quite markedly, the acetylation comes to the end within half an hour. Small lumps of unchanged starch are left, which can no more be attacked on further addition of acetic anhydride. This is centrifuged away and the somewhat turbid, viscous solution, after evaporating off some acetic acid, is poured in ice water. The acetylated product separates out as a flocky precipitate, while zinc chloride and others dissolve in the water. By repeatedly rubbing with fresh water the solid is reduced to a fine powder, which is nearly free from impurity. Yield 60 gr. of the well-dried substance, that is 90% of the theoretical amount.

For the purification the dried acetyl starch was dissolved in hot chloroform and alcohol was added until a turbidity appeared. When allowed to cool, the acetyl starch separated out as a white fine powder, which was filtered and washed with alcohol. Although the pure chloroform solution was left, crystals did not appear, but a thin film like that of collodium was formed on the wall of the vessel.

This acetylated starch is different in several points (temperature of decomposition, solubility, specific rotation, etc.) from any of those already described⁽²⁾; when heated in a capillary tube, it sinters at 258° and slowly decomposes over 270°. It dissolves in acetic acid, chloroform (free from alcohol), pyridine, acetic anhydride, conc. sulphuric acid (remaining without a slight decomposition for 20 minutes), ethylene bromide, bromoform, and phenol, far more readily at higher temperatures. The solution is clear when dilute but more or less turbid when over 2-5 percent. It is tolerably

-
- (1) "Starch soluble Merck" is used. It is never "soluble" and swells up with hot water just like the potato starch washed with dilute alkali and dilute acid. The specific rotation (190°) and the content of ash (0.18%) is also the same.
- (2) F. Pregl; M. Bergmann and E. Knehe, loc. cit. in which detailed descriptions on its properties, especially on its solubility are deficient.

soluble in acetone, acetic ether, and toluene, less in benzene and carbon tetrachloride, far less in petroleum ether, ether, and alcohols, and almost insoluble in water. In hot toluene it is fairly soluble; a beautiful fluorescence is observed when its solution is allowed to cool.

For the analysis the purified acetyl starch was again dissolved in a mixture of toluene and acetone on the water bath, precipitated with alcohol, and dried at 110° in vacuum over phosphorus pentoxide.

0.1930 gr. of subst. gave 0.3513 gr. CO₂ and 0.0988 gr. H₂O. (Found: C=49.64; H=5.73. C₆H₇O₅(C₂H₃O)₃ requires C=49.98; H=5.60%)

The acetyl value was determined by saponifying the substance with a known amount of 1/4 n-NaOH, in warm acetone solution,⁽¹⁾ the excess of alkali being titrated with 1/10 n-HCl, using phenolphthalein as the indicator.

0.1660 and 0.2000 gr. of subst. required 6.93 and 8.37 c.c. of 1/4 n-NaOH respectively. (Found: CH₃CO=44.8; 44.9. C₆H₇O₅(CH₃CO)₃ requires CH₃CO=44.8%)

Optical study was made in readily dissolving solvents:

$$[\alpha]_D^{25} = \frac{2.86^\circ \times 100}{1.680 \times 1} = 170.2^\circ \text{ (in chloroform),}$$

$$[\alpha]_D^{25} = \frac{2.72^\circ \times 100}{1.695 \times 1} = 160.4^\circ \text{ (in acetic acid),}$$

$$[\alpha]_D^{14} = \frac{2.35^\circ \times 100}{1.471 \times 1} = 159.6^\circ \text{ (in pyridine).}$$

The Saponified Product of the Triacetyl Starch. Saponification was carried out most easily in the following way: dried triacetyl starch (2 gr.) was dissolved in hot toluene (40 c.c.) and sodium ethylate (0.6 gr. Na in 15 c.c. C₂H₅ OH) was added. Reaction occurred immediately, the vessel being filled with a gelatinous product, which was dissolved on addition of water. The excess of alkali was neutralized with acetic acid. The liquid separated into two layers, namely, a layer of turbid aqueous solution and that of clear toluene, which was separated. The former solution was filtered, evaporated at 40° in vacuum to a small volume (35 c.c.) and poured in methyl alcohol (250 c.c.). The saponified product separated out as a white precipitate, which was filtered and washed with alcohol. It was again dissolved in water and precipitated with alcohol.

(1) In fact, the substance was first dissolved in a small amount of boiling toluene, then acetone (50 c.c.) was added and warmed on the water bath.

It is an amorphous white somewhat hygroscopic powder, forming a clear solution with water when dilute, but an opaque solution when concentrated. It gives a pure indigo-blue colour with iodine and does not reduce Fehling's solution. For analysis it was dried at 110° and 1 mm. over phosphorus pentoxide.

0.2122 gr. of subst. gave 0.3430 gr. CO₂ and 0.1203 gr. H₂O. (Found : C=44.08 ; H=6.34. C₆H₁₀O₅ requires C=44.42 ; H=6.22%)

$$[\alpha]_D^{21} = \frac{1.98^\circ \times 100}{1.046 \times 1} = 189.3^\circ \text{ (in water).}$$

The original starch used for the acetylation has the specific rotation :

$$[\alpha]_D^{27} = \frac{1.76^\circ \times 100}{0.926 \times 1} = 190.0^\circ \text{ (in water).}$$

Though the saponified product of the acetyl starch is identical with the original starch in the specific rotation and the colouration with iodine, they differ in the following respect : the former dissolves in water, while the latter swells up with hot water, forming the paste.

These two starches cannot, however, be regarded as essentially different, because according to Samec the fraction of starch containing phosphate (amylopectin) forms the paste, while that free from phosphate (amylose) dissolves in water without forming the paste, thus the cause of forming the paste may be attributed to the component containing phosphate⁽¹⁾; and indeed, when the phosphate is removed, the amylopectin gives a homogenous, not opaque solution⁽²⁾ and on the other hand, when phosphoric acid is introduced into the amylopectin which is deprived of its phosphate, there is formed a product similar to the original amylopectin.⁽³⁾ Now, the present saponified product of the triacetyl starch has been found to contain no phosphate, so it is quite natural that it should be more soluble than the original starch containing phosphate. That the soluble saponified product may be essentially "soluble starch" is shown by the fact that its clear solution yields a light cloudy precipitate when left a few days, as is usually the case with the clear solution of amylose.

Finally, it must be mentioned that it was confirmed that during the process of acetylation the starch remains unchanged (in the specific rotation, the colouration with iodine, the behaviour towards water etc.) before the acetyl group is introduced, even under the treatments of gelatinization with zinc chloride solution and heating in acetic acid.

(1) M. Samec and v. Hoeft, *Kolloidchem. Beih.*, **5** (1913), 141.

(2) M. Samec, *Kolloidchem. Beih.*, **6** (1914), 23.

(3) M. Samec and A. Mayer, *Comp. rend.*, **173** (1921), 321.

From these facts it may be said that the starch is not changed (essentially) by the treatments of the acetylation and the saponification.

The Reacetylation of the Saponified Product. Acetyl group was introduced again into the saponified product of the triacetyl starch by the same method, the acetylated product being purified as before. When heated in a capillary tube it sinters at 257° and gradually decomposes over 270°. The specific rotation is also the same as before :

$$[\alpha]_D^{28} = \frac{2.90^\circ \times 100}{1.698 \times 1} = 170.6^\circ \text{ (in chloroform),}$$

$$[\alpha]_D^{28} = \frac{2.86^\circ \times 100}{1.785 \times 1} = 160.2^\circ \text{ (in acetic acid).}$$

It is concluded, therefore, that the saponified product of the acetyl starch can be brought back to the original acetyl starch by introducing the acetyl group without causing a change.

The Molecular Weight of the Triacetyl Starch.

Since Karrer published an idea that starch may be a polymerised product of a relatively small molecule such as maltose anhydride,⁽¹⁾ other polysaccharides naturally have come to be believed as similarly composed of such small elementary molecules. This idea was directly demonstrated with inulin by the cryoscopic study in liquid ammonia,⁽²⁾ and with various polysaccharides further direct confirmations of this idea were brought forward also by the cryoscopic investigations of their acetyl derivatives. The conclusions are striking: The triacetyl derivative of cellulose,⁽³⁾ lichenin⁽³⁾⁽⁸⁾, inulin⁽⁴⁾⁽⁸⁾, glycogen⁽⁶⁾, salep-mannan,⁽⁶⁾ amylose⁽⁸⁾ in *acetic acid*, and that of amylopectin⁽⁸⁾, amylose⁽⁷⁾ in *phenol*, all may be considered quite unexpectedly to exist as a single molecule of triacetyl hexosan (mol. wt. 288).

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- (1) P. Karrer and C. Nägeli, *Helv. Chim. Acta*, **4** (1921), 263; P. Karrer, *Naturw.*, **9** (1921), 399; P. Karrer, *Z. angew. Chem.*, **35** (1922), 85.
 - (2) L. Schmid and B. Becker, *Ber.*, **58** (1925), 1968; Reichlen and Nestle, *Ber.*, **59** (1926), 1159. From these experiments inulin is considered to exist as such a small molecule as fructose-disaccharide anhydride, but it was recently reported by L. Schmid and G. Bilowitzki (*Monatsch.*, **48** (1927), 163) that no elevation of the boiling point of piperidine is observed upon the addition of inulin.
 - (3) K. Hess and Schultze, *Ann.*, **448** (1926), 99.
 - (4) K. Hess and Stahn, *Ann.*, **455** (1927), 104.
 - (5) K. Hess and Stahn, *Ann.*, **455** (1927), 115.
 - (6) H. Pringsheim and G. Liss, *Ann.*, **460** (1928), 32.
 - (7) M. Bergmann and E. Knehe, *Ann.*, **452** (1927), 141.
 - (8) M. Bergmann, E. Knehe and v. Lippmann, *Ann.*, **458** (1927), 93.

Of these experiments it must, however, be remarked that the depressions of the freezing point giving such a small molecular weight, could be observed only at low concentrations (ca. 0.05–0.5%) and only when observations were carried out not immediately but several hours or several days after dissolving the substance. The investigators explain this phenomenon as due to the disassociation of the large molecule of polysaccharides, which proceeds quite slowly and only in dilute solutions.

Expecting to obtain similar results also in other media which are neutral and indifferent to the substance, the author has made cryoscopic studies of the triacetyl starch in ethylene bromide, bromoform and camphor, and also in acetic acid and phenol, and ebullioscopic studies in chloroform, acetone, and acetic acid. The result is that, in almost all solvents, the depressions of freezing point or the elevations of boiling point were exceedingly small at high or low concentrations. As a comparative study, the author has observed also the freezing point depression of the solvent caused by the acetyl derivative of some simple carbohydrates as glucose and saccharose, the results of which have confirmed that the triacetyl starch exists all the same as a huge, polymerised molecule compared with such simple carbohydrates, even in dilute solutions.

The Cryoscopy. The freezing vessel is so constructed that measurements may be carried out in high vacuum. The stirrer is made of platinum wire, to the top of which a ring of tin-plate is attached, and moved up and down by means of an electro-magnet.⁽¹⁾ The results of the cryoscopic studies of the triacetyl starch using ethylene bromide, bromoform, camphor, and acetic acid as solvent, are given in the following tables.

1. *Ethylene bromide.* Freezing point 9.5° . $K=120$.⁽²⁾ It has proved to be an excellent cryoscopic solvent for the acetyl starch, owing to the fairly large dissolving power, the large cryoscopic constant and the ease of purification. It was purified by shaking with a soda solution, drying with calcium chloride, and distilling two times in the space shut off from the moist air. Boiling point 131.2° . After introducing the solvent or the substance, the freezing vessel was evacuated so as to expel the moist air. Evacuation has also the benefit of hastening the dissolving of the substance.

(1) Ostwald-Luther, "Physiko-chemische Messungen," (1925), p. 332.

(2) The mean value of several observers'. See P. Walden, "Molekulargrößen von Elektrolyten in nichtwässrigen Lösungsmitteln," (1923), p. 208.

Triacetyl starch (gr.)	Ethylene bromide (gr.)	Conc. (%)	Depression (degree)	Mol. wt.	Remarks.	
					subst. dissolved at:	observed after: (hour)
{0.0148	17.6	0.084	0.004	(2600)		1
{0.0148	17.6	0.084	0.003	(3400)		3
{0.0305	23.5	0.130	-0.005		60°	3
{0.0305	23.5	0.130	0.000			21
0.0266	17.6	0.151	0.004	(4500)	80°	0.5
{0.0718	20.8	0.345	0.010	4100	70°	4.5
{0.0718	20.8	0.345	0.010	4100		22
{0.0748	17.6	0.425	0.010	5100		1
{0.1524	17.6	0.865	0.017	6200		3
0.174	19.4	0.897	0.019	5600		20
0.159	17.6	0.903	0.021	5100		1
{0.181	19.3	0.938	0.021	5350	60°	6
{0.181	19.3	0.938	0.022	5100		26
{0.114	17.6	0.648	0.010	8050		0.3
{0.463	17.6	2.63	0.051	6400		3
{0.463	19.8	2.34	0.057	4900		3.5
{0.463	19.8	2.34	0.048	5850		22
β -Pentaacetyl glucose (mol. wt. 390)						
0.151	17.6	0.859	0.251	410		
0.187	17.6	1.062	0.311	410		
0.189	19.8	0.954	0.272	420		
Octaacetyl saccharose (mol. wt. 678)						
0.055	17.6	0.313	0.063	600		
0.073	16.0	0.456	0.085	643		
0.163	17.6	0.926	0.170	652		
0.314	19.8	1.58	0.281	677		
0.489	19.8	2.48	0.422	702		

2. *Bromoform*. Freezing point 7°. K=144.

Triacetyl starch (gr.)	Bromoform (gr.)	Conc. (%)	Depression (degree)	Mol. wt.
0.120	19.4	0.620	0.017	5020
0.144	22.3	0.646	0.020	4650
0.321	22.3	1.44	0.041	5050
β -Pentaacetyl glucose (mol. wt. 390)				
0.148	19.5	0.759	0.276	408
Octaacetyl saccharose (mol. wt. 678)				
0.157	19.4	0.809	0.174	671

3. *Camphor*. Melting point 178°. $K=400$.

Triacetyl starch (gr.)	Camphor (gr.)	Conc. (%)	Depression (degree)	Mol. wt.
0.1140	0.671	17.0	3.5	1940
0.0674	0.400	16.5	3.1	2120
0.0316	0.553	5.70	1.5	1520

In spite of high concentrations the molecular weight has come out considerably small, about one-third of that found in other solvents. This is probably due to the disassociation of the large molecule caused by the high temperature.

4. *Acetic acid*. Freezing point 16°. $K=39$. Measurements were carried out in high vacuum, as Hess⁽¹⁾ and Bergmann⁽²⁾ have recommended in the cryoscopy with the polysaccharide acetate in this solvent, in order to avoid irregular depressions which would occur otherwise.

Triacetyl starch (gr.)	Acetic acid (gr.)	Conc. (%)	Depression (degree)	Mol. wt.	Remarks. observed after: (hour)
{ 0.0110	26.2	0.042	0.007	230	19
{ 0.0110	26.2	0.042	0.010	160	72
{ 0.0400	15.7	0.254	0.120	82	20
{ 0.0400	15.7	0.254	-0.090		72
{ 0.0870	21.0	0.414	0.080	195	21
{ 0.0870	21.0	0.414	-0.050		72
0.0987	22.6	0.436	0.009	1900	1
0.0480	7.40	0.648	0.012	2100	0.5
{ 0.284	24.1	1.13	0.072	610	22
{ 0.284	24.1	1.13	0.008	5600	72
0.100	7.10	1.48	0.030	1910	0.5
β -Pentaacetyl glucose (mol. wt. 390)					
0.0747	7.40	1.09	0.100	393	

It is seen in the table that soon after dissolving the substance, depressions were quite small, then became larger and after more hours became again smaller and in some cases even elevations were observed. The pure

(1) *Ann.*, **448** (1926), 99.

(2) *Ann.*, **458** (1927), 93.

solvent itself being sometimes found to change its freezing point with the time,⁽¹⁾ the author dare not attribute these changes of depression to the dissociation of the acetyl starch or to the reassociation of the elementary molecules thus disassociated.

5. *Phenol*. Freezing point 40°. $K=79$. Phenol is more difficult to manipulate than acetic acid; the freezing temperature even of pure phenol fell quite irregularly by 0.02° or more at every freezing with all precautions,⁽²⁾ but no particular depression was observed due to the addition of a small amount (0.3%) of the triacetyl starch.

From the above studies it may be clearly pointed out that such solvents which are not indifferent but sensitive to moisture and air as acetic acid and phenol, quite unlike the neutral solvents, being very liable to cause too large (improper) depressions, are regarded to be no adequate cryoscopic solvent, especially for higher polysaccharides because depressions caused by the addition of them may be considerably small in any case.

The Ebullioscopy. The results of the ebullioscopic studies of the triacetyl starch using acetic acid and chloroform as solvent are given in the following tables. These solvents, being somewhat difficult to manipulate, and elevations of boiling point being quite small, the values of molecular weight are not very reliable, but it is clearly shown that the triacetyl starch has a molecular weight far larger than the (β -pentaacetyl) glucose.

1. *Acetic acid*. Boiling point 118°. $K=25$.

Triacetyl starch (gr.)	Acetic acid. (cc.)	Conc. (%)	Elevation (degree)	Mol. wt.
0.911	19.5	4.67	0.016	7100
0.911	22.0	4.14	0.017	6100
0.911	23.0	3.96	0.020	5000
<i>β-Pentaacetyl glucose</i> (mol. wt. 390)				
0.690	11.5	6.00	0.330	455
0.690	17.5	3.94	0.240	416
0.690	19.8	3.52	0.241	368

- (1) Therefore, in the above determinations the freezing point was also observed of the pure solvent in parallel with the solutions.
- (2) Purified phenol with a definite boiling point was frozen in high vacuum.

2. *Chloroform*. Boiling point 61.2°. K=26.

Triacetyl starch (gr.)	Chloroform (cc.)	Conc. (%)	Elevation degree)	Mol. wt.
0.732	17	4.30	0.017	6900
0.732	1	3.48	0.014	6500
0.732	25	2.93	0.011	6900
0.732	26	2.81	0.013	5600
0.117	10	1.17	0.005	6100

3. *Acetone*. Boiling point 56°. K=22. No measurable elevation of the boiling point was observed on the addition of the triacetyl starch.

The results of the above cryoscopic and ebullioscopic investigations give a conclusion that *the triacetyl starch possesses, at least in some neutral solvents, a molecular weight as large as or more than that of 18 times polymerised anhydro-glucose triacetate*⁽¹⁾ [$\{C_6H_7O_5(C_2H_3O)_3\}_{18} = 288 \times 18 = 5184$] and does not seem to be disassociated to the elementary molecules merely by diluting or by leaving the solution, as other investigators⁽²⁾ have observed by doing so.

However, in further more dilute solutions the complete disassociation may well take place, but that can no longer be confirmed with the present cryoscopic method.

The author wishes to express his appreciation to Professor T. Soda for his kind advices and inspiring encouragements in the course of this investigation.

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(1) This result is strongly in favour of A. Pictet's estimation that soluble starch (least polymerised) should be tri-hexahexosan (18 times polymerised anhydro-glucose) considering from the specific rotation of some lower polyhexosans. *Helv. Chim. Acta.*, 9 (1926), 33.

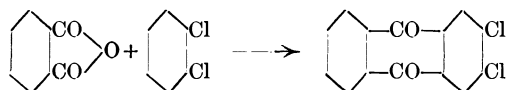
(2) K. Hess; M. Bergmann, loc. cit.

KONDENSATION VON PHTALSÄUREANHYDRID MIT *o*-DICHLORBENZOL.

Von Munenari TANAKA und Naozo TANAKA.

Eingegangen am 10. Oktober 1928. Ausgegeben am 28. November 1928.

Ueber die Kondensation von Phtalsäureanhydrid mit *o*-Chlorphenol ein Zusatz von Borsäure in Schwefelsäure, habe ich schon kurz berichtet. Brauch ich aber Aluminiumchlorid statt Schwefelsäure nach der Vorschrift von Ullmann⁽¹⁾, bekomme ich bei 130° einen schwach gelben Körper, der nach meiner Meinung wahrscheinlich 3'-4'-Oxychlorbenzophenoncarbonsäure⁽²⁾ ist, die ich aber leider nicht in reinen Zustand habe bringen können. Degegen kann *o*-Dichlorbenzol leicht mit Phtalsäureanhydrid mittelst Aluminiumchlorid kondensiert werden. Hierbei entsteht bei 115° 3'-4'-Dichlorbenzophenoncarbonsäure (2), was ganz genau mit der Arbeit von Sprent⁽²⁾ übereinstimmt. Steigert man jedoch die Temperatur bis auf 150° so bekommt man wie mit Druck bei 130° 2-3-Dichloranthrachinon.



Bei dieser Gelegenheit möchte ich noch etwas zu meiner letzten Arbeit⁽³⁾ hinzufügen. Nachdem Herr Mizoshita dieselbe nochmals genau wiederholt hat, fand er folgendes: Er erhitzt *o*-Chlorphenol und Phtalsäureanhydrid mit Borsäure und Schwefelsäure 1 Stunde auf 240° und treibt dann die Temperatur $\frac{1}{2}$ Stunde lang auf 255°, hierbei entsteht ein Gemisch von Alizarin und noch etwas unverändertes 1-Oxy-2-chloranthrachinon. Erhitzt er schliesslich 3 Stunden lang auf 255°, so bildet sich Purpurin.

Experimentaler Teil (bearbeitet bei N. Tanaka)

1. 3'-4'-Dichlorbenzophenoncarbonsäure (2). 15 gr. *o*-Dichlorbenzol, 15 gr. Phtalsäureanhydrid und 30 gr. gepulvertes Aluminiumchlorid werden innig gemischt und erwärmt, hierbei entweicht reichlich Chlorwasserstoff, und die Masse färbt sich bräunlich und wird dickflüssig. Unter Rühren wird dann die Schmelze einige Stunden auf 120° erhitzt. Nach dem Erkalten werden Wasser und verdünnte Salzsäure hinzugefügt und geringe Mengen von unverbrauchtem *o*-Dichlorbenzol mit Dampf abgeblasen. Der

(1) Ullmann, D.R.P. 282493.

(2) Sprent u. Dodd, B.R.P. 204528 (1923). Vergl. Heller u. Schülke, *Ber.*, **41** (1908), 3627.

(3) M. Tanaka, *Proc. Imp. Acad.*, **3** (1927), 82 u. 345; B.R.P. 245584, 256068.

braun gelbe Rückstand wird mit 5 proz. Natronlauge erwärmt. Es scheidet sich die 3'-4'-Dichlorbenzophenoncarbonsäure (2) auf Zusatz von Salzsäure als kristallinisch erstarrende Masse aus. Der aus Benzol mit Tierkohle umkristallisierte Körper zeigt dem Schmelzpunkt 190° und stellt weisse Nadeln dar.

Analyse: 17.30 mg. Subst. gaben 35.80 mg. CO₂ und 3.75 mg. H₂O. (Gefunden: C=56.5; H=2.40. Berechnet für C₁₄H₈O₃Cl₂: C=57.0; H=2.71%)

Diese lösen sich gut in heissem Alkohol, Benzol und Eisessig. Erwärmt man die 3'-4'-Dichlorbenzophenoncarbonsäure (2) mit der 10 fachen Menge Schwefelsäure auf dem Wasserbade, so färbt die Lösung bald gelb unter Bildung von 2-3-Dichloranthrachinon, welche bei 265° schmelzen.

2. **2-3-Dichloranthrachinon.** Kondensiert man *o*-Dichlorbenzol mit Phtalsäureanhydrid in Gegenwart von Aluminiumchlorid bei 150° für einige Stunden oder mit Druck bei 130° und arbeitet das Gemisch nach der in oben angegebenen Methode auf, so erhält man gelbe Kristalle. Der aus Eisessig mit Tierkohle umkristallisierte Körper zeigt den Schmelzpunkt 265–267°, gelbe Nadeln bildend.

Analyse: 7.35 mg. Subst. gaben 16.45 mg. CO₂ und 1.20 mg. H₂O. (Gefunden: C=61.3; H=1.82. Berechnet für C₁₄H₆O₂Cl₂: C=61.7; H=2.17%).

Schmilzt man diese Körper mit Kali, so entsteht Alizarin, was Kirscher⁽¹⁾ schon erwähnte.

3. **1-2-4-Trioxyanthrachinon.** 10 gr. *o*-Chlorphenol, 32 gr. Phtalsäureanhydrid, 20 gr. Borsäure und 160 gr. konz. Schwefelsäure werden auf 255° erhitzt. Die erhaltene Mischung wird, ohne zu kühlen, in kaltes Wasser gegossen, ausgekocht, abfiltriert und getrocknet. Hierauf wird der Farbstoff mit kochendem Toluol extrahiert und daraus umkristallisiert. Aus Eisessig nochmal umkristallisiert, werden rote Nadeln dargestellt. Schmelzpunkt 256°.

Analyse: 13.49 mg. Subst. gaben 32.4 mg. CO₂ und 3.20 mg. H₂O. (Gefunden: C=65.7; H=2.63. Berechnet für C₁₄H₈O₆: C=65.7; H=3.13%).

Nov. 1927.

Zentrallaboratorium, Dairen.

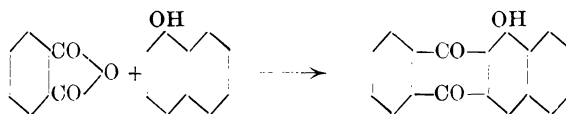
(1) Kirscher, *Ann.*, **245** (1887), 348; Grandmougin, *Compt. rend.*, **173** (1921), 717; Liebermann, *Ber.*, **35** (1902), 1780.

DEHYDRATE WIRKUNG VON JAPANISCHER SÄUREERDE IN ANTHRACHINONREIHE.

Von Munenari TANAKA und Susumu WATANABE

Eingegangen am 10. Oktober 1928. Ausgegeben am 28. November 1928.

Ueber die dehydrate Wirkung von Alumina und Silica wurde zuerst von Meilhe⁽¹⁾ und seinen Mitarbeitern in 1918 veröffentlicht und ähnliche Arbeiten sind mit Japanischessäureerde von H. Inoue⁽²⁾ und K. Ono⁽³⁾ gemacht worden. Wir haben diese Methode über Anthrachinonderivate angewandt und fanden: Die dehydrate Wirkung von Erde ist nicht so stark wie bei Aluminiumchlorid⁽⁴⁾, doch kann Hydrochinon leicht mit Phtalsäureanhydrid mittelst Erde bei 260° kondensiert werden. Brauchen wir aber Brentzkatechin statt Hydrochinon, bekommen wir eine ganz geringe Menge von Hystazarin und Alizarin. Bei Anwendung von Pyrogallol auf diese Weise erhalten wir kein Anthrachinonderivat, sondern Triphenylmethanfarbstoff, nämlich Gallein (bei Aluminiumchlorid resultiert Anthragallol) und schliesslich bekommt man aus α -Naphtol auf diese Weise, α -Oxynaphtacenchinon⁽⁵⁾, dagegen nicht aus β -Naphtol.



Bei dem oben angegebenen Beispiel können wir folgendes feststellen: Die Hydroxylgruppe in der *p*-Stelle (oder α -Stelle) hat verwandschaft mit der Carbonylgruppe, d. h. α -Oxyanthrachinon das tautomere *o*-chinoid⁽⁶⁾ Form besitzt.

Experimentaler Teil (bearbeitet von S. Watanabe).

1. **Chinizarin (1-4-Dioxyanthrachinon).** Wir erhitzen 20 gr. Phtalsäureanhydrid und 10 gr. Japanische-säureerde (wasserfrei) gut gemischt und treiben die Temperatur auf 350°, 10 gr. Hydrochinon und ein Gemisch von Phtalsäureanhydrid und Erde (10 gr.) wird wechselweise bei 260–270° unter gutem Rühren hinzugefügt. Die Mischung wird nun so lange auf 260° erhitzt, bis eine Probe sich in verdünnter Natronlauge mit violetter

(1) Mailhe und Goden, *Compt. rend.*, **160** (1918), 467 u. 564.

(2) H. Inoue, diese Zeitschr., **1** (1926), 157, 177, 197, 219.

(3) K. Ono, diese Zeitschr., **1** (1926), 248.

(4) D.R.P. 289345.

(5) Deicher u. Weizman, *Ber.*, **36** (1903), 547 u. 719.

(6) M. Tanaka, *Proc. Imp. Acad.*, **3** (1927), 83; C. Graebe, „Chinone“, S. 405.

Farbe löst. Nach dem Erkalten wird die Schmelze zerkleinert, mit Wasser gekocht, filtriert und getrocknet. Der Rückstand wird mit siedendem Alkohol extrahiert. Beim Erkalten scheidet sich das Chinizarin als schöne orange Blätterchen aus. Smpt., 194°.

Analyse: 16.40 mg. Subst. gaben 42.10 mg. CO₂ und 4.55 mg. H₂O. (Gefunden: C=69.9; H=3.19. Berechnet für C₁₄H₈O₄: C=70.0; H=3.33%).

2. **Hystazarin und Alizarin.** Erhitzt man, wie in Beispiel 1 angegeben, 30 gr. Phtalsäureanhydrid, 10 gr. Brentzkatechin und 20 gr. Erde, so erhält man ein Gemisch von Hystazarin und Alizarin. Beide werden bekannter Weise mit Toluol getrennt. Hystazarin zersetzt bei über 310°. Alizarin Schmilzt bei 289°.

3. **α-Oxynaphtacenchinon.** 20 gr. Phtalsäureanhydrid, 5 gr. α-Naphtol werden mit 10 gr. Erde innig verrieben, das Gemisch unter gutem Rühren schnell bei 250–260° erhitzt, bis eine Probe sich in alkoholischem Kali schön kirschrot löst. Nach dem Erkalten wird die Schmelze pulverisiert und mit siedendem Alkohol extrahiert um unverändertes Rohmaterial zu entfernen. Der Rückstand wird aus Nitrobenzol extrahiert, wobei sich α-Oxynaphtacenchinon als schön gelbe Nadeln, welche bei 303° schmelzen, ausscheidet. Zur Analyse aus Nitrobenzol umkristallisiertes Oxynaphtacenchinon wurde nochmals aus Toluol umkristallisiert und bei 110° getrocknet.

Analyse: 7.01 mg. Subst. gaben 20.10 mg. CO₂ und 2.20 mg. H₂O. (Gefunden: C=78.4; H=3.49. Berechnet für C₁₈H₁₀O₃: C=78.8; H=3.65%).

α-Monoxynaphtacenchinon ist in heissem Nitrobenzol oder Toluol leicht löslich, schwerer in Alkohol oder Eisessig. In konzentriertem Alkali ist es unlöslich, in alkoholischem Kali löst es sich schön kirschrot, in Schwefelsäure mit schön karminroter Farbe.

Sept. 24, 1928.

Zentrallaboratorium, Dairen.

CRYOSCOPIC STUDIES ON THE TRANSITION POINTS OF THE
COMPOUNDS OF ORGANIC SOLVENTS WITH SALTS. I.

By Hajime OSAKA.

Received October 10, 1928. Published November 28, 1928.

In the ordinary cryoscopy, we observe the univariant behaviour of systems of two components, a solvent and a solute. Similarly any univariant system formed of three or more components is also applicable to this purpose.

and in analogy to the lowering of the freezing point of a single solvent, the lowering of the transition point by the addition of foreign substances was first investigated by Löwenherz⁽¹⁾ in the case of sodium sulphate decahydrate. He found that the transition point of the decahydrate into anhydrous salt, i. e. 32.38°C., was lowered by foreign substances by amount which gave 32.6 as the molecular depression referred to 100 gr. of the decahydrate. After this investigation similar studies were carried out for salt hydrates by other investigators⁽²⁾ in succession. Among them Dawson and Jackson state that "the referring of the concentration to 100 gr. of the solution in which the foreign substance is contained is a more convenient and correct procedure." In general, however, if a transition point of a salt hydrate at which it is transformed into an anhydride is to be used, the writer considers it more convenient to prefer the molecular depression referred to 100 gr. of water to that referred to 100 gr. of the molten hydrate or the solution. In the case of sodium sulphate, for example, since 322 gr. of the decahydrate contain 180 gr. of water, the constant referred to 100 gr. of water becomes $32.6 \times \frac{180}{322} = 18.2$, and the experiment may be carried out without using the molten hydrate.

This sort of cryoscopy can be applied also to the systems in which an organic liquid, instead of water, is present as solvent. In case an organic liquid with a strong solvent power has too low a freezing point to be used in the ordinary cryoscopy, this method would be convenient if the solvent combines with some salt to form a compound, of which transition point is in the neighbourhood of room temperatures. In this respect acetone comes in consideration first of all. This excellent solvent has its freezing point at -94.6°C., but forms some acetone compounds with salts, such as $\text{NaI} \cdot 3\text{CH}_3\text{COCH}_3$ [trans. pt. = 25.5°C.] and $\text{HgCl}_2 \cdot \text{CH}_3\text{COCH}_3$ [trans. pt. = 20.7°C.]. At the transition point these compounds are converted into the solid salt and the saturated solution. The results of the cryoscopic measurements carried out with these two systems are given in the following.

It is supposed that salt $[X]$ combines with n molecules of acetone to form acetone compound $[X \cdot nA]$. In Fig. 1 curve (1) represents vapour pressures of the acetone compound dissociating to the salt and acetone vapour, and curve (2) vapour pressures of the system consisting of the salt, the

(1) Löwenherz, *Z. physik. Chem.*, **18** (1895), 70.

(2) Van't Hoff & Dawson, *Z. physik. Chem.*, **22** (1897), 598; Van't Hoff & Müller, *Ber.*, **31** (1898) 2206; Morgan & Benson, *J. Am. Chem. Soc.*, **29** (1907), 1168; Morgan & Owen, *ibid.*, 1439; Dawson & Jackson, *J. Chem. Soc.*, **93** (1908), 344.

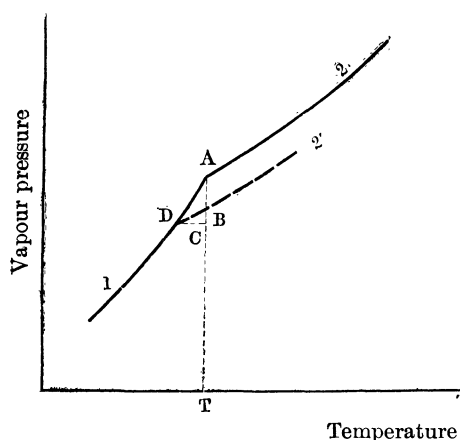


Fig. 1.

solution saturated with respect to the salt and acetone vapour. Curve (2') shows vapour pressures of the system (2) when another solute is dissolved in it. Here it is assumed that the solute does not appreciably affect the solubility of the salt. A is the transition point, D the lowered transition point, DC the depression of the transition point (ΔT), and AB the depression of vapour pressure (Δp). Applying the Clapeyron-Clausius equation to this case, the following expression is derived for the depression ΔT ,

$$\Delta T = \frac{RT^2}{q_1 - q_2} \frac{\Delta p}{p}, \dots \dots \dots (1)$$

where R is the gas constant, T the transition point, q_1 the molar heat of evaporation of acetone from the acetone compound and q_2 the molar heat of evaporation of acetone from the saturated solution. The changes which occur in these two kinds of evaporation may be shown by the following equations.

$$[X.nA] = [X] + nA - nq_1,$$

$$[X + cA] = [X] + cA - cq_2.$$

where $[]$ represents a solid phase, $()$ a liquid phase, and a gaseous phase is shown by symbols only. The composition of the liquid phase is given by c , the number of mols of acetone which contains one mol of the salt. From these equations the expression for the melting of the compound is obtained.

$$[X.nA] = \frac{c-n}{c} [X] + \frac{n}{c} (X + cA) - n(q_1 - q_2).$$

Now the molar heat of fusion H can be written as

$$H = n(q_1 - q_2). \dots \dots \dots (2)$$

If the concentration of the saturated salt solution and that of the same saturated solution which contains the other solute are given by N and N' in mole fractions, and the corresponding vapour pressures by p and p' respectively,

$$\text{then } \frac{p'}{p} = \frac{N'}{N}, \text{ accordingly } \frac{\Delta p}{p} = \frac{p - p'}{p} = 1 - \frac{N'}{N}.$$

If 100 gr. of acetone contains x gr. of the solute (mol. wt. = M),

$$N' = \frac{\frac{100}{58.05}}{\frac{100}{58.05} \left(1 + \frac{i}{c}\right) + \frac{x}{M}} \quad \text{and} \quad N = \frac{\frac{100}{58.05}}{\frac{100}{58.05} \left(1 + \frac{i}{c}\right)},$$

where i is the degree of dissociation of the salt in the solution plus unity and 58.05 is the molecular weight of acetone. Here also it is assumed that i and c are not appreciably affected by the existence of the solute. From the above relations follows

$$\frac{\Delta p}{p} = \frac{\frac{x}{M}}{\frac{100}{58.05} \left(1 + \frac{i}{c}\right) + \frac{x}{M}}, \quad \dots \quad (3)$$

where x/M in the denominator may be neglected within the limits of experimental error.

Substituting equations (2) and (3) in equation (1), the following expression for the depression ΔT is obtained.

$$\Delta T = \frac{nRT^2}{H} \cdot \frac{\frac{x}{M}}{\frac{100}{58.05} \left(1 + \frac{i}{c}\right)}.$$

If w gr. of the solute is present in W gr. of acetone,

$$\frac{x}{M} = \frac{100}{W} \cdot \frac{w}{M}.$$

Hence

$$\Delta T = \left(\frac{RT^2}{H} \cdot \frac{58.05}{100} \cdot \frac{nc}{(c+i)} \right) \cdot \frac{100}{W} \cdot \frac{w}{M}, \quad \dots \quad (4)$$

where the term contained in the outer brackets is independent of the nature of the solute and represents the molecular depression K of the transition point referred to 100 gr. of acetone.

Apparatus and Method of Procedure. A Beckmann⁽¹⁾ apparatus with a magnetic stirrer was used for the cryoscopic experiments. The cooling bath was kept constant within 0.1°, and the temperature was such that the convergent temperature was 0.1–0.2° below the transition point. To a known amount of acetone was added a sufficient amount of salt to form the satura-

(1) Beckmann, *Z. physik. Chem.*, **44** (1903), 169.

ted solution and the solid phase, at a temperature one or two degrees above the transition point. The system was then supercooled, a crystal of the new phase, e. g. the acetone compound, was added and the constant maximum temperature was observed. The ordinary procedure of cryoscopy followed, and the molecular depression K was calculated by the expression (4): $\Delta T = K \frac{100 w}{W M}$, introducing the correction for x/M which was eliminated in equation (3).

Preparation of Materials. Acetone was dehydrated by K_2CO_3 , and was distilled twice with precaution against moisture.

Sodium iodide was recrystallized from water as $NaI \cdot 2H_2O$ and was dehydrated by heating. Jones⁽¹⁾ describes that the solution of NaI in acetone was coloured deeply yellow. He supposed at first that this was due to the liberation of iodine but a test with starch paste showed that no free iodine was present, and consequently the yellow colour was ascribed presumably to some reaction between acetone and NaI . According to my experiment, however, the solution was colourless even when saturated and boiled. After some time this turned somewhat yellowish but not deeply yellow.

Mercuric chloride of the Japanese Pharmacopœia was used after drying without further purification.

Other substances were purified by sublimation or recrystallization.

Results. *The case of $NaI \cdot 3CH_3COCH_3$.* The lowerings of the transition point of this system caused by the addition of each of eight organic compounds were measured, and the results are given in the following table.

TABLE 1.

(1) Solute: Naphthalene (mol. wt. = 128).

Wt. of acetone (W) in gr.	Wt. of NaI in gr.	Wt. of solute (w) in gr.	Observed depression of trans. pt. ΔT	Molecular depression K
23.7	12.0	0.374	0.307	25.1
23.8	11.5	0.769	0.617	24.7
23.7	12.0	0.769	0.642	25.7
23.6	12.7	0.770	0.601	23.9
23.6	12.7	1.408	1.105	24.3
Mean				24.7

(1) Jones, *Am. Chem. J.*, **27** (1902), 21.

(2) Solute: Camphor (mol. wt.=152).

W	Wt. of NaI	w	ΔT	K
23.8	11.7	0.585	0.366	22.8
23.7	12.7	0.585	0.369	22.9
23.8	11.7	1.275	0.793	22.8
23.7	12.7	1.275	0.787	22.6
23.8	11.7	1.659	1.025	22.8
Mean				22.8

(3) Solute: Benzoic acid (mol. wt. = 122).

W	Wt. of NaI	w	ΔT	K
23.8	11.5	0.432	0.347	23.5
23.8	11.5	0.429	0.349	23.7
23.8	11.5	0.860	0.689	23.6
23.8	11.5	0.862	0.714	24.4
Mean				23.8

(4) Solute: Acetanilide (mol. wt.=135).

W	Wt. of NaI	w	ΔT	K
31.5	16.0	0.475	0.273	24.7
23.7	—	0.486	0.358	23.7
23.8	11.5	0.474	0.362	24.7
23.7	11.7	0.485	0.375	25.0
23.7	12.7	0.487	0.380	25.2
23.8	11.5	0.889	0.692	25.4
23.7	12.7	0.892	0.705	25.7
Mean				24.9

(5) Solute: *p*-Nitraniline (mol. wt.=138).

W	Wt. of NaI	w	ΔT	K
23.7	—	0.443	0.326	24.2
23.7	12.7	0.443	0.337	25.0
23.7	—	0.586	0.441	24.8
23.7	—	0.737	0.558	25.0
23.7	—	1.332	1.018	25.5
Mean				25.1

(6) Solute : Phthalic anhydride (mol. wt.=148).

<i>W</i>	Wt. of NaI	<i>w</i>	ΔT	<i>K</i>
23.8	11.5	0.529	0.346	23.3
23.7	11.5	0.528	0.349	23.4
23.8	11.5	1.055	0.687	23.3
23.7	11.5	1.054	0.691	23.4
Mean				23.4

(7) Solute : Benzil (mol. wt.=210).

<i>W</i>	Wt. of NaI	<i>w</i>	ΔT	<i>K</i>
23.8	11.5	0.682	0.302	22.3
23.4	11.5	0.665	0.312	23.2
23.7	11.5	0.682	0.323	23.7
23.8	11.5	1.081	0.488	22.8
23.7	12.7	1.081	0.501	23.3
23.4	11.5	1.074	0.509	23.5
23.7	11.5	1.081	0.511	23.8
Mean				23.3

(8) Solute : Coumarin (mol. wt.=146).

<i>W</i>	Wt. of NaI	<i>w</i>	ΔT	<i>K</i>
31.6	15.0	0.514	0.270	24.4
23.7	11.5	0.508	0.350	24.1
31.6	15.0	1.023	0.533	24.3
23.7	11.5	1.025	0.684	23.5
Mean				24.1

The mean of these values of the molecular depression is 24.0. The value for each solute differs from the mean at most by amount of 5%, so that this system can practically be used for the cryoscopic measurement.

The values of the transition point obtained in these experiments are given in Table 2, where (I) is the readings of the Beckmann thermometer and (II) is the corresponding temperatures (corrected) in Celcius degree.

TABLE 2.

I	II	I	II	I	II	I	II
3.522	25.48	3.466	25.43	3.500	25.46	3.515	25.48
3.530	25.49	3.498	25.46	3.490	25.45	3.491	25.45
3.501	25.46	3.499	25.46	3.505	25.47	3.499	25.46
3.517	25.48	3.477	25.44	3.501	25.46	3.534	25.50
3.507	25.47	3.493	25.46	3.497	25.46	3.502	25.47
Mean							25.46

This value is 0.2° lower than 25.7°C. obtained by other authors⁽¹⁾ from the solubility data.

The case of $\text{HgCl}_2 \cdot \text{CH}_3\text{COCH}_3$. Aten⁽²⁾ gave 13°C. as the transition point of this compound, but according to the measurements similar to the previous case, this point is 20.7°C. , 8° higher than the above value as shown in Table 3. Aten's value may be perhaps effected by the insufficiency of the solubility data used in the graphical determination of this point.

TABLE 3.

I	4.818	4.824	4.850	4.789	4.856	4.870
II	20.61	20.64	20.67	20.61	20.68	20.69

The mean : 20.66°C.

In this case if freezing and melting were repeated with the same solution it showed gradual lowering of the transition point, so that this cannot practically be used for the cryoscopic purpose. The acetone solution of HgCl_2 was at first colourless, but became yellowish in a few hours, deeply yellow in the next day, and it turned gradually from brown to a brownish black viscous liquid. The molecular depression was determined always using the solutions newly prepared. The results were not so concordant as in the case of sodium iodide. As the mean value of the molecular depression 24 was obtained.

Summary.

1. The lowering of the transition point, at which $\text{NaI} \cdot 3\text{CH}_3\text{COCH}_3$ loses acetone, by the dissolution of foreign substances has been studied and the molecular depression referred to 100 gr. of acetone has been determined

(1) Macy & Thomas, *J. Am. Chem. Soc.*, **48** (1926), 1547. Wadworth & Dawson, *J. Chem. Soc.*, 129 (1926), 2784.

(2) Aten, *Z. physik. Chem.*, **54** (1906), 121.

as 24.0. The transition point has been also determined as 25.5°C. The method may be regarded as the cryoscopy using acetone with an artificially elevated melting point and can be used practically for the molecular weight determination.

2. A similar study has been carried out with $\text{HgCl}_2 \cdot \text{CH}_3\text{COCH}_3$. The molecular depression has been determined as 24 and the transition point as 20.7°C. This system shows, however, some inaccuracy so that it can hardly be applied to the practical cryoscopy.

The writer wishes to express his hearty gratitude to Prof. M. Katayama, under whose kind guidance this work has been carried out.

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ON THE CHEMICAL CONSTITUTION OF CLUPANODONIC ACID.

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The unsaturated acids occurring in natural oils and fats, which have hitherto been investigated by chemists for their chemical constitution, are chiefly those of the oleic acid series. Of the acids of higher unsaturation we may count only linolic, elaeostearic, and linolenic acids. As to the so-called highly unsaturated acids ($C_nH_{2n-8}O_2$ and $C_nH_{2n-10}O_2$ series), which occur commonly and abundantly in marine animal oils, no reliable investigation has yet been performed, and at present we lack nearly wholly the definite knowledge of their constitution. The present paper deals with the constitution of clupanodonic acid, $C_{22}H_{34}O_2$, which is one of the most important and typical members of such series.

More than thirty years ago W. Fahrion⁽¹⁾ reported that on oxidising "jecoric acid", $C_{18}H_{30}O_2$, by Hazura's oxidation method he was unable to obtain hydroxylated acids, except volatile acids and carbon dioxide. Presumably his "jecoric acid" was impure highly unsaturated acids. R. Majima and T. Okada⁽²⁾ attempted to investigate the constitution of clupanodonic acid, but the acid obtained by debrominating the polybromide of the fatty acids of Japanese sardine oil was found not to be a simple chemical compound; so they were obliged to give up their original project. Recently from a study on the fatty acids of a "South Georgia whale oil", E. F. Armstrong and T. P. Hilditch⁽³⁾ made an interesting statement that in C_{20} and C_{22} acid groups there was slightest evidence of the occurrence of an ethylenic linkage between the carboxyl group and the ninth carbon atom in the chain. This conclusion appears, however, to be too hasty, inasmuch as they did not isolate the C_{20} and C_{22} highly unsaturated acids, but oxidized the mixed acid fractions respectively. But there must have been present a large amount of less unsaturated acids, such as $C_{20}H_{38}O_2$ (gadoleic acid?) and cetoleic acid, $C_{22}H_{42}O_2$, in the fractions, whereas the amount of the highly unsaturated acids was small.⁽⁴⁾ The statement propounded by R. R. McGregor with G. D. Beal⁽⁵⁾ on the limit of unsaturation in menhaden oil is

(1) *Chem. Ztg.*, **17** (1893), 521.

(2) *J. Tokyo Chem. Soc.*, **35** (1914), 13.

(3) *J. Soc. Chem. Ind.*, **44** (1925), 180 T.

(4) Y. Toyama, *Chem. Umschau*, **31** (1924), 221, 238; **33** (1926), 293; **34** (1927), 19.

(5) *J. Am. Chem. Soc.*, **48** (1926), 3150.

essentially an amplification of the conclusion of Armstrong and Hilditch. Nor were they able to arrive at definite results by the decomposition of the ozonides of the highly unsaturated acids.

The present writer has succeeded to isolate nearly pure clupanodonic acid by his lithium-salt-acetone method.⁽¹⁾ The method of bromination and debromination hitherto used for the isolation of polyethylenic acids, such as linolic and linolenic acids, has a drawback that there is no certain proof that the position of ethylenic linkage is not displaced by such violent chemical treatments. The comparatively mild treatments (saponification, esterification, distillation under diminished pressure) of the writer's method are probably free from the above defect.

Clupanodonic acid readily absorbs ozone in chloroformic solution forming ozonide. But this compound appears to be unstable and it has been found difficult to obtain it in pure state. On decomposing the ozonide with water, the nearly whole part of the decomposition products go to the solution leaving only a small amount of an oily insoluble substance. By the writer's experiments, there were found as volatile decomposition products acetaldehyde, propionaldehyde, and carbon dioxide, and as non-volatile product a comparatively large amount of succinic acid. Azelaic acid and other higher dibasic acids, or their semialdehydes were found not to be present, at least appreciably. According to Armstrong and Hilditch's statement, a marked amount of such compounds should be present in the decomposition products.

As the decomposition products of clupanodonic acid ozonide were mainly soluble in water, so for the confirmation of the product containing the carboxyl group, the amyl ester of the acid was ozonised and decomposed with water. By this means an insoluble decomposition product containing the esterified carboxyl group was obtained, which on saponification yielded succinic acid. So the product contained four carbon atoms; therefore the first ethylenic linkage in clupanodonic acid is situated between fourth and fifth carbon atoms counting from the carboxyl group. Acetaldehyde and carbon dioxide were likely formed as the secondary decomposition products of malonic dialdehyde, or semialdehyde of malonic acid. Now calculating from the amount of the carbon dioxide formed, the atomic group, $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$, contained in a molecule of clupanodonic acid is probably one. Conjugate double bonds are probably not present, since neither glyoxal nor glyoxylic acid was detected, and also no trace of oxalic acid was found; also by heating clupanodonic acid with metallic sodium and alcohol, no lowering of the iodine value was observed. The presence of triple bonds is negated by the fact that the iodine value of clupanodonic acid and the

(1) *Chem. Umschau*, 27 (1920), 229; 33 (1926), 285.

bromine content of its bromine addition compound closely agree with the numbers calculated from five double bonds.

By the above mentioned results, it has been confirmed that the molecule of clupanodonic acid consists of the following atomic groups: (1) $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}=\text{}$, (2) $=\text{CH}\cdot\text{CH}_2\cdot\text{CH}=\text{}$, (3) $=\text{CH}\cdot(\text{CH}_2)_2\text{CH}=\text{}$, and (4) $=\text{CH}\cdot(\text{CH}_2)_2\text{COOH}$. As to some of the arrangement of these groups, no definite data have yet been obtained. But according to a recent investigation of Y. Toyama,⁽¹⁾ cetoleic acid, $\text{C}_{22}\text{H}_{42}\text{O}_2$, which occurs widely distributed in marine animal oils and has 22 carbon atoms alike to clupanodonic acid, has been proved to be $\Delta^{11,12}$ dococenic acid. From the fact that linolic and linolenic acids have each an ethylenic linkage between ninth and tenth carbon atoms as oleic acid, so if we assume an analogy exists in the case of clupanodonic and cetoleic acids, it is not unreasonable to think that clupanodonic acid has an ethylenic linkage between eleventh and twelfth carbon atoms as cetoleic acid. Then the possible arrangement of carbon atoms in the molecule of clupanodonic acid is $\text{C}_3=\text{C}_4=\text{C}_4=\text{C}_4=\text{C}_3=\text{C}_4$ (right end—carboxyl) and $\text{C}_3=\text{C}_4=\text{C}_4=\text{C}_3=\text{C}_4=\text{C}_4$ (ibid.), so that the constitution of clupanodonic acid will be one of the following two formulae:⁽²⁾

- (1) $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_2\cdot\text{CH}:\text{CH}\cdot(\text{CH}_2)_2\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}(\text{CH}_2)_2\cdot\text{COOH}$.
- (2) $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}(\text{CH}_2)_2\cdot\text{CH}:\text{CH}(\text{CH}_2)_2\cdot\text{COOH}$.

As the decomposition products of clupanodonic acid ozonide are very complicated, no pretension can be insisted for not overlooking some important compounds. And as some of the arrangement of the atomic groups is hypothetical, the above formulae have only been proposed provisionally. Further investigations may verify or correct them. As to the arrangement of the atomic groups, the examination of the decomposition products of partially hydrogenated clupanodonic acid may probably furnish some clue for its definite confirmation.

Experimental Part.

(I) **Material.** The fatty acids of a Japanese sardine oil from Hokkaidō were treated by the lithium-salt-acetone method, and the highly unsaturated acids so obtained were changed to the methyl esters and fractionated under 5 mm. pressure. The fraction boiling at $217\text{--}226^\circ$ was taken as the methyl ester of clupanodonic acid. It was saponified and the accompanying small

(1) *Chem. Umschau*, **35** (1928), 20.

(2) That clupanodonic acid has straight chain structure is already known by the formation of behenic acid on hydrogenation.

amount of unsaponifiable matter was removed, and finally oxidised acids were separated by means of petroleum ether. The clupanodonic acid thus refined had the following properties: $d_4^{15}=0.9410$, neutralisation value 170.7, iodine value 388.8, $n_D^{15}=1.5057$. Calculated for $C_{22}H_{34}O_2$: neutr. value 169.8, iodine value 384.3.

The specific gravity and refractive index were respectively higher than those of previously obtained. Whether these are due to the presence of more highly unsaturated acids (e. g. $C_{22}H_{32}O_2$), or the previously isolated clupanodonic acid was still contaminated with less unsaturated acids, is not certain. In the present experiments the above sample was, however, accepted as pure clupanodonic acid.

(II) **Preparation of Clupanodonic Acid Ozonide.** Five gr. of clupanodonic acid were dissolved in 50 c.c. of chloroform, and on cooling with ice and salt a current of ozonised oxygen (washed with 5% NaOH solution and sulphuric acid; ozone content ca. 5%) was passed into the solution at the rate of 6 litres per hour during for 5 hours. Then the chloroform was distilled off under a diminished pressure at about 30°. By keeping the ozonide over night under diminished pressure it was decomposed with water. The yield of the ozonide was 11–12 gr. per 5 gr. of the acid, so that it was much higher than that calculated for normal ozonide (8.6 gr.). This was probably due to the difficulty of removing last part of the solvent. The ozonide appeared also to be unstable, so it was decomposed next day without further keeping.

The ozonide thus obtained formed a pale yellow, elastic, linoxyn-like mass, and burned explosively when heated. Great difficulty was experienced in its elementary analysis, and the result was very unsatisfactorily. The carbon content was found apparently much higher; this was probably caused by adhered chloroform.

(III) **Decomposition of Clupanodonic Acid Ozonide with Water.** To the ozonide obtained from 5 gr. of clupanodonic acid, 100 c.c. of water were added and heated on a water bath in the current of hydrogen. The flask was fitted with a condenser, and the latter in turn combined to the following three flasks, through which the evolved gas together with hydrogen may pass without leakage: (a) 50 c.c. of water (cooled with ice), (b) 150 c.c. of ca. N/3 Ba(OH)₂ solution, (c) 50 c.c. of the same. As the ozonide by rapid heating with water made an explosion-like decomposition, so the mixture was at first very carefully warmed to 65–70°, and kept somewhat long time at this temperature, and then the temperature was gradually raised till the water in the bath boiled. The ozonide decomposed with evolution of gas, firstly floated on the surface of water as a viscous oily liquid, this then gradually went to the solution, and finally there remained at the bottom of

the flask a small amount of a brownish insoluble liquid substance. The solution became discoloured by degrees and assumed a brownish orange-yellow colour. The above operation was five times repeated and so totally the ozonide obtained from 25 gr. of clupanodonic acid was decomposed.

(1) *Volatile Decomposition Products.* The volatile products caught in the flasks *a*, *b* and *c* were examined.

(a) The solution in the flask *a* showed marked aldehyde reactions. A colourless liquid collected at the bottom of the flask was found to be admixed chloroform. With *p*-nitrophenylhydrazine and hydrochloric acid the solution gave a bright orange-yellow precipitate, which on twice recrystallisations from 50% alcohol, formed orange-yellow needles of melting point 116.5–117°. 0.1138 gr. subst. gave 0.2308 gr. CO₂ and 0.0581 gr. H₂O; 0.1425 gr. subst. gave 28.9 c.c. nitrogen (23°, 756 mm.). (Found: C=55.31; H=5.71; N=22.61. C₈H₉O₂N₃ requires C=53.60; H=5.07; N=23.47. C₉H₁₁O₂N₃ requires C=55.93; H=5.74; N=21.76%). The percentage of carbon and hydrogen corresponded nearly to those of the nitrophenylhydrazone of propionaldehyde, but that of nitrogen was the mean of those of the compounds of acetaldehyde and propionaldehyde. The presence of the two aldehydes was proved by (1) diethylamine and sodium nitroprusside (acetaldehyde), and (2) skatole reaction (propionaldehyde).

(b) The precipitate formed in the flasks, *b* and *c*, appeared to consist of barium carbonate. The carbon dioxide was possibly formed as the secondary decomposition product of the ozonide. For its quantitative determination, the following procedure was adopted. The excess of Ba(OH)₂ was firstly neutralised with N/2 hydrochloric acid using phenolphthalein as indicator. Then adding methylorange as indicator the farther addition of hydrochloric acid was made until the white precipitate was dissolved and the solution assumed a clear pink colour. From the amount of HCl used for the second titration, the weight of carbon dioxide was calculated.

The determination was repeated with the ozonide obtained from each 5 gr. of clupanodonic acid. As the most reliable number, the writer obtained 0.838 gr., i.e. ca. 16.8% for clupanodonic acid. The presence of acetaldehyde and carbon dioxide in the decomposition products of the ozonide is, as already stated, probably due to the secondary decomposition of malonic dialdehyde, or semialdehyde of malonic acid. So it may be inferred that in the molecule of clupanodonic acid there are contained atomic groups, such as =CH·CH₂·CH= or =CH·CH₂·COOH. If there is only one such group, =CH·CH₂·CH= (40) in one molecule of clupanodonic acid (330.3), then the carbon dioxide formed by the decomposition (CH·CH₂·CH→CO₂+CH₃·CHO) must be 13.3% for clupanodonic acid. The number obtained above (16.8%) was somewhat greater than it, but if we assume the presence of two such

groups, then the amount of carbon dioxide is too small, so that the number of the group contained is probably only one. That the carboxyl is not contained in the group was confirmed by the experiments made on the ozonide of the amyl ester of clupanodonic acid (see below).

(2) *Non-Volatile Decomposition Products.* The aqueous solution of the decomposition products obtained from each 5 gr. of clupanodonic acid ozonide was treated as follows:

Firstly the solution was filtered through a filter paper, thereby the insoluble substance was left. The filtrate was twice treated with each 150 c.c. of ether, the ether layer separated from the lower aqueous solution (*C*), and treated with sodium bicarbonate solution in a separating funnel. The upper ether solution was separated, dehydrated with anhydrous magnesium sulphate and the ether distilled off. The thereby remaining portion (*A*) consisted chiefly of aldehydic constituents. The sodium bicarbonate extract was acidified with dilute hydrochloric acid and exhausted with ether (three times with each 100 c.c.) and then ether distilled off; by this operation the acidic constituents (*B*) were obtained. The yield of the products was found difficult to determine exactly, chiefly owing to their volatility. But roughly speaking the following numbers were obtained:

From the ozonide of 10 gr. of clupanodonic acid: *A* only 0.3 gr.; *B* 3.2 gr.; *C* or the aqueous solution separated from ether layer was evaporated under a diminished pressure, and about 5 gr. of the residue was obtained. On the evaporation the solution became discoloured, and a substance difficultly soluble in ether or water was produced. This was probably the resinified products of aldehydes. The insoluble oily substance firstly formed was about 0.6 gr.

(a) Part *A*. On distilling off the ether, an orange-yellow liquid was left. This was difficultly soluble in water; it formed with nitrophenylhydrazine a dark reddish viscous precipitate, and with semicarbazide hydrochloride a semicarbazone (?) of m.p. above 200°. As no definite derivative was obtained, the substance was analysed as follows: 0.1373 gr. subst. gave 0.3033 gr. CO₂ and 0.0946 gr. H₂O. (Found C=60.25, H=7.71%). If we consider the substance to be an aldehyde or its polymerised product, so succinic dialdehyde C₄H₆O₂ (C=55.78, H=7.03%) or glutaric dialdehyde C₅H₈O₂ (C=59.96, H=8.06%) correspond somewhat to it.

(b) Part *B*. From the ozonide of 25 gr. of clupanodonic acid, about 8 gr. of this part was obtained. It formed an orange-yellow liquid not solidified by cooling in ice. It was firstly distilled at the ordinary pressure, thereby at the bath temperature of 140° the distillation began. At the bath temperature of 160° (dist. temp. ca 110°) the distillation was interrupted. The distillate (*B1*) amounted to 1.9 gr.; a pale yellow pungent liquid of

$n_D^{20}=1.3700$ and of aldehydic reaction. Then the distillation was continued under 6 mm. pressure. Up to the bath temp. of 180° and the distillation temp. of 135° , 0.8 gr. of distillate (*B2*) was obtained; this was a pale orange-yellow liquid. By this temperature, the indication of decomposition was observed; so the distillation was stopped. The residue (*B3*), 4.2 gr.; a dark brown viscous liquid mixed with crystals.

B1. This was dissolved in alcohol and titrated with $\text{Ba}(\text{OH})_2$ solution (acid value found was 520); it was then exhausted with ether to remove aldehydic compounds. The barium salt obtained by evaporating the alcohol and water contained 55.4% Ba, $((\text{C}_2\text{H}_3\text{O}_2)_2\text{Ba}$ requires $\text{Ba}=53.79\%$); so the acid seemed to consist of acetic acid. But judging from somewhat high distillation temperature, there appeared the presence of propionic acid (b.p. 141°) to be likely.

B2. Showed a marked aldehyde reaction and had the acid value 425. On oxidising it with alkaline potassium permanganate solution, white crystals were obtained. On carefully washing with ether, they melted at 177.5° and the mixed melting point test with succinic acid⁽¹⁾ showed $180-181^\circ$. So this substance was confirmed to be succinic acid. The crude product probably contained succinic semialdehyde.

B3. Showed also a marked aldehyde reaction. By treating it with ether, a brown tarry insoluble substance was left; it was, however, completely soluble in acetic ether. On oxidising it with alkaline potassium permanganate solution, a yellowish white crystalline semisolid was obtained with a yield of 70%; the white crystals obtained by treating it with ether to remove the liquid part melted at about 177° and the mixed test with succinic acid was $179-180^\circ$. So the substance was confirmed to be also succinic acid.

(c) Part *C*. On distilling off the ether under a diminished pressure, a dark brownish viscous substance was obtained. It was soluble in acetone and acetic ether, but on treatment with ether, a black-brown viscous substance was left. This was probably polymerised aldehydes. As the substance did not distil under diminished pressure when heated to a bath temperature of 150° , so the content of the flask was dissolved out with acetone (thereby much amount of tarry substance was separated). The substance left on evaporating off the acetone was dissolved in a little water and exhausted with ether. On evaporating off the ether, an extract was obtained with a yield of about 54%. This was a mixture of crystals and an orange-yellow liquid. It was then treated with cold ether to remove the liquid part, and the crystals were dissolved in acetic ether, and decolourised with animal charcoal. On concentration and cooling, the solution deposited white crystals,

(1) Merck, m. p. $183-183.5^\circ$. In this and in the following experiments, always equal parts were mixed.

which melted at 182–182.5° and had the neutralisation value 936. The mixed test with succinic acid was 182°. So the substance was succinic acid.

On directly oxidising the original substance with alkaline potassium permanganate solution, white crystals of m.p. 182–182.5° (mixed test with succinic acid 181.5–182°) and the neutr. value 934 were obtained. Its elementary analysis gave the following result: 0.1187 gr. subst. gave 0.1786 gr. CO₂ and 0.0574 gr. H₂O. (Found: C=41.04; H=5.41. C₄H₆O₄ requires C=40.66; H=5.12%). The substance was, therefore, confirmed to be succinic acid.

Beside the above mentioned experiments the insoluble oily substance, which was formed in a small amount on decomposing the ozonide with water, was oxidised, and a substance (white crystals) resembling azelaic acid was obtained, but owing to its small quantity it was found difficult to confirm it with certainty. If this was really azelaic acid, then the oily substance was probably formed from ozonides of some less unsaturated acids, which were contaminated in the sample of clupanodonic acid.

(IV) **Decomposition of the Amyl Ester Ozonide of Clupanodonic Acid.** This experiment was undertaken to confirm the position of the ethylenic linkage nearest to the carboxyl group. As the decomposition products of clupanodonic acid ozonide with water are nearly wholly soluble in water, in order to settle the question the writer has esterified the acid with a sparingly soluble alkyl group and ozonised it. By decomposition with water, the atomic group containing the esterified carboxyl group will be obtained as an insoluble product and its nature may be identified. Apparently a higher alkyl group would be better for the purpose, but as it is difficult to expel it, so amyl group was chosen for the experiment.

Six gr. of clupanodonic acid, 24 gr. of amyl alcohol containing 2.5% of HCl and 30 c.c. of ether were heated in a flask with a reflux condenser on a water bath in the current of carbon dioxide for one hour and then the content of the flask was washed with water, taken up with ether, and dried with anhydrous sodium sulphate. The ether was then distilled off and the excess of amyl alcohol was removed under a diminished pressure. The amyl ester so prepared had the acid value of 9.9 showing some presence of free acid, but as it had the saponification value 139.5, nearly corresponding to that (140.1) of amyl clupanodonate, C₂₁H₃₃COOC₅H₁₁, it was used as the material for ozonisation.

Five gr. of the amyl ester were dissolved in 50 c.c. of chloroform and ozonised. The yield of the ozonide, which contained still some amount of the solvent, was 9.8 gr. It was an orange-yellow viscous liquid. On heating it with 80 c.c. of water on a water bath for one hour, there was observed an appreciable amount of an orange-yellow insoluble oily liquid formed at the

bottom of the flask. The supernatant liquid was filtered off and the oily substance was again heated with 8 times of water in order to complete the decomposition. The oily substance finally left was 2.46 gr. corresponding to about 49% of the original ester.

This substance was dissolved in alcohol and titrated with alcoholic potash to neutralisation, and then on adding water the aldehydic or neutral substances were extracted with ether, and the aqueous solution was acidified with hydrochloric acid and exhausted with ether. On distilling off the ether, about 32% of a dark brownish liquid of the neutralisation value 255 was obtained (neutr. value of mono-amyl ester of succinic acid $\text{HOOC}(\text{CH}_2)_2\text{COOC}_5\text{H}_{11} = 298.2$). Then the substance was saponified with an excess of alcoholic potash and acidifying with hydrochloric acid the free acid was extracted with ether. The extract consisted of a mixture of liquid and crystals. This was treated with ice-cooled ether to remove the liquid part and then the crystals were dissolved in acetic ether and decolourised with animal charcoal. On concentrating the solution and cooling with ice, crystals were obtained, which melted at 177° and had the neutralisation value 605. As this seemed still to contain some amount of neutral substances, so the neutralised solution was evaporated to dryness, dissolved in water and treated with ether. To the aqueous solution, dilute hydrochloric acid was added, and the free acid was exhausted with ether. The solid remaining on evaporating off the ether melted at $179\text{--}180^\circ$ and had the neutr. value 944. The mixed test with succinic acid was $181\text{--}181.5^\circ$. So this substance was identified as succinic acid.

Then the firstly extracted aldehydic part (ca. 42%) was examined. It was oxidised with an alkaline potassium permanganate solution and the product was neutralised with alcoholic potash, and the neutral substances extracted with ether. From the lower aqueous solution on decomposing it with hydrochloric acid there was obtained by exhausting with ether a substance probably consisting of mono-amyl ester of succinic acid. It was a pale yellow liquid of the neutr. value 294. On saponification the free acid was obtained; it was refined by means of acetic ether. The substance formed white crystals of m.p. 180. The mixed test with succinic acid was $181\text{--}181.5^\circ$; so this was also succinic acid.

From the above results it has been concluded that among the decomposition products of the ozonide of amyl clupanodonate, that part which is combined with the amyl group is succinic acid. Therefore the ethylenic linkage nearest to the carboxyl group in the molecule of clupanodonic acid is situated between fourth and fifth carbon atoms counting from the carboxyl group. The calculated percentage of succinic mono-amyl ester to be obtained from amyl clupanodonate is 47%. The yield of 49% nearly corresponded to it.

The Tokyo Imperial Industrial Laboratory.

**AN INTERPRETATION OF THE REARRANGEMENTS OF
PINACONES AND TERTIARY AMINO-ALCOHOLS
FROM THE ELECTRON THEORY OF
VALENCY (THEORETICAL PART).**

By **Masao MIGITA.**

Received November 15, 1928. Published December 28, 1928.

Introduction. Since the discovery of triphenyl-methyl by Gomberg, the theory of "Valenzbeanspruchung" has played an important rôle in the theoretical line of the organic chemistry. Consequently the comparison of firmness of attachment of organic radicals to an element affords one of the most interesting subjects. Thus, J. v. Braun⁽¹⁾ compared the firmness of attachment of organic radicals to nitrogen atom by the reaction products of tertiary amines and cyanogen bromide; and K. v. Auwers⁽²⁾ in his "quaternary indazolium salt method" by its thermal decomposition products.

As to the method to compare the "affinity requirement" of organic radicals to carbon atom Skraup and his co-workers proposed two methods, namely, "oxazol-⁽³⁾" and "carbinol method."⁽⁴⁾ In the former, the reaction velocity of ring rupture of substituted benzoxazoles is compared, and the latter is based on the assumption that basicity of various carbinols is due to the varying affinity of carbinol-carbon atom. Another method is given by Meerwein⁽⁵⁾ during studies on pinacolone-rearrangement. As is well known, pinacone, when dehydrated, easily yields pinacolone by intramolecular rearrangement. The mechanism of this transformation was the subject of discussion over twenty-five years, but finally Tiffeneau⁽⁶⁾ concluded that this rearrangement occurs together with elimination of water through a "frac-

tion of a molecule,"

$$\begin{array}{c} \text{—O} \\ | \\ \text{R} \diagup \text{C} \text{—} \text{C} \diagdown \text{R} \\ | \quad | \\ \text{R} \quad \text{R}' \end{array}$$

which cannot be isolated. Then in the

(1) *Ber.*, **55** (1922), 3165; **56** (1923), 1573. $\text{R}'\text{R}''\text{R}'''\text{N} + \text{BrCN} = \text{R}'\text{R}''\text{N} \cdot \text{CN} + \text{R}'''\text{Br}$.

(2) *Ber.*, **53** (1925), 1360. $[\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ \diagdown \quad \diagup \\ \text{NR}' \end{array}] \cdot \text{X} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ \diagdown \quad \diagup \\ \text{NR}' \end{array} \text{N} + \text{R}''\text{X}$ or

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ | \\ \text{N} \end{array} \text{NR}' + \text{R}'\text{X}.$$

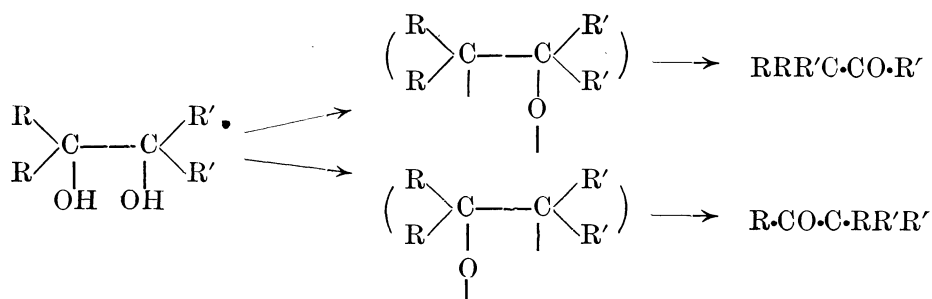
(3) *Ann.*, **419** (1919), 1; *Ber.*, **55** (1922), 1080. $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{CR} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{NHCOR} \\ \diagdown \quad \diagup \\ \text{OH} \end{array}$

(4) *Ber.*, **55** (1922), 1074.

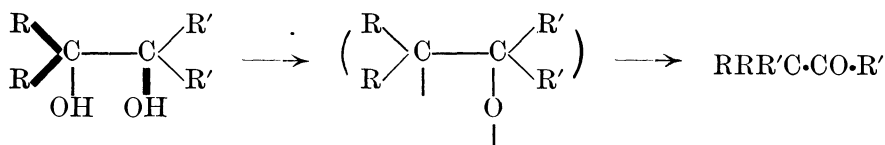
(5) *Ann.*, **419** (1919), 121.

(6) *Compt. rend.*, **143** (1906), 687.

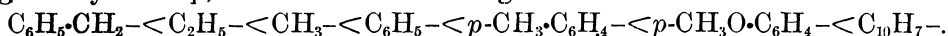
case of unsymmetrically substituted pinacones, we may have :



and the direction of the rearrangement may be determined by the firmness of the union of the two hydroxyl radicals. Now, Meerwein considered that the carbon atom combined to hydrocarbon radicals which possess greater "affinity requirement" leaves less affinity to combine with hydroxyl group, consequently it is this hydroxyl radical which is removed on dehydration. The scheme of the rearrangement is as follows :

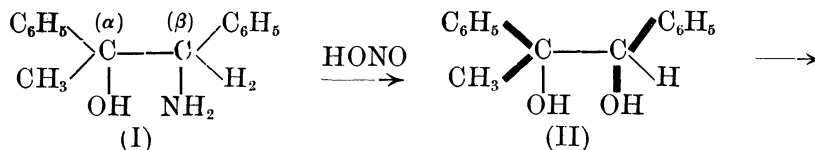


where thick bar denotes the greater "affinity requirement." By the studies on various pinacones he determined the relative "affinity requirement" of several radicals. In addition to his result, taking in consideration those given by Skraup,⁽¹⁾ we have the following series :



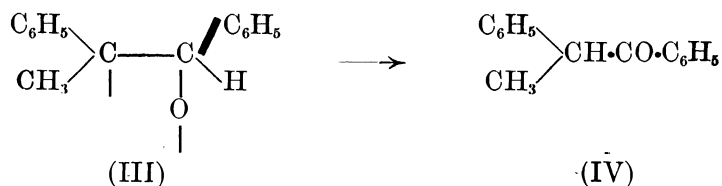
Action of nitrous acid on tertiary amino-alcohols. Few years ago McKenzie⁽²⁾ found that tertiary amino-alcohols, when acted by nitrous acid, do not give normally glycols but they perform a kind of pinacolone rearrangement which he proposed to call *semipinacolinic deamination*. Now, if we attempt to predict the result of this transformation by the theory of "affinity requirement" as in the case of pinacones, we will be surprised at unexpected results (see Table below).

For example, in the case of β -amino- α β -diphenyl- α -methyl-ethyl-alcohol (I), we expect the following course of reaction :

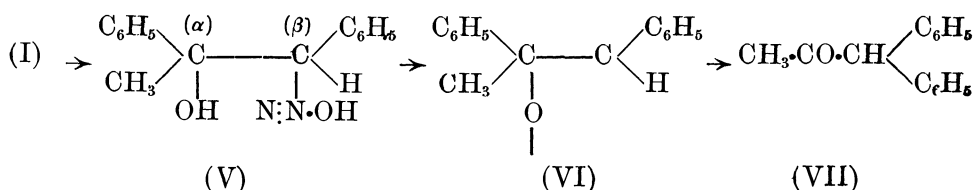


(1) Loc. cit.

(2) McKenzie and Richardson, *J. Chem. Soc.*, **123** (1923), 79.



The transformation from (III) to (IV) is explained thus: out of the two substituents attached to β -carbon atom the less firmly combined hydrogen atom migrates to α -carbon atom, giving phenyl-methyl-acetophenone (IV). But the product actually obtained is diphenyl-acetone $(\text{C}_6\text{H}_5)_2\text{CH} \cdot \text{CO} \cdot \text{CH}_3$. In order to explain this contradiction, McKenzie supposed that the transformation occurs in the following manner:



Owing to the easiness with which nitrogen is eliminated, the hydroxyl group attached to α -carbon atom is more firmly bound than is the nitrogen atom attached to β -carbon atom, so that the linkage $\text{-N}_2\text{OH}$ would be severed first. Though this assumption accounts for the mode of dehydration in all the semipinacolinic deamination of amino-alcohols, it can not explain why certain tertiary amino-alcohols such as γ -amino- $\alpha\alpha\gamma$ -triphenyl-propyl alcohol,⁽¹⁾ $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{C}_6\text{H}_5$ and β -amino- β -phenyl- $\alpha\alpha$ -diethyl-ethyl alcohol,⁽²⁾ $(\text{C}_2\text{H}_5)_2\text{C}(\text{OH}) \cdot \text{CH}(\text{NH}_2) \cdot \text{C}_6\text{H}_5$ behave normally toward nitrous acid, giving corresponding glycols. Moreover, as the theory of "affinity requirement" can not explain why in the above example, phenyl group which is to be considered more firmly bound than methyl group migrates in the last stage of the reaction (VI) $\rightarrow$ (VII), we must admit the provision that a certain migrational aptitude is conceded to each radical, this property being not necessarily concomitant with its saturation capacity.⁽³⁾ This means that the theory of "affinity requirement" can not foretell the products of semipinacolinic deamination of tertiary amino-alcohols, except those of the type $\text{R}_2\text{C}(\text{OH}) \cdot \text{CHR}'(\text{NH}_2)$.

(1) McKenzie and Richardson, *J. Chem. Soc.*, **123** (1923), 85.

(2) *Ibid.*, **1927**, 571.

(3) Tiffeneau and Lévy, *Compt. rend.*, **176** (1923), 312.

TABLE 1.
The Products of Semipinacolinic Deamination of Tertiary
Amino-alcohols.

No.	Tert. amino-alcohol.	Actual product.	Product expected from	
			Electron theory	Affinity-requirement
1.	Ph ₂ C(OH)·CHPh(NH ₂)	Ph ₂ CH·CO·Ph	The same.	The same.
2.	PhMeC(OH)·CHPh(NH ₂)	Ph ₂ CH·CO·Me	The same.	The same.
3.	PhEtC(OH)·CHPh(NH ₂)	Ph ₂ CH·CO·Et	The same.	PhEtCH·CO·Ph
4.	PhNapC(OH)·CHPh(NH ₂)	Ph ₂ CH·CO·Nap	PhNapCH·CO·Ph	PhNaCH·CO·Ph
5.	Ph ₂ C(OH)·CHMe(NH ₂)	PhMeCH·CO·Ph	The same.	Ph ₂ CH·CO·Me
6.	Ph ₂ C(OH)·CHBzl(NH ₂)	PhBzlCH·CO·Ph	The same.	Ph ₂ CH·CO·Bzl
7.	Ph ₂ C(OH)·CH ₂ (NH ₂)	PhCH ₂ ·CO·Ph	The same.	Ph ₂ CH·CHO
8.	PhAnisC(OH)·CH ₂ (NH ₂)	AnisCH ₂ ·CO·Ph	The same.	PhAnisCH·CHO
9.	PhNapC(OH)·CH ₂ (NH ₂)	NapCH ₂ ·CO·Ph	The same.	PhNapCH·CHO
10.	Bzl ₂ C(OH)·CHMe(NH ₂)	BzlMeCH·CO·Bzl	The same.	— *
11.	Bzl ₂ C(OH)·CHPh(NH ₂)	BzlPhCH·CO·Bzl	The same.	— *

Ph = Phenyl, Me = Methyl, Et = Ethyl, Nap = Naphthyl, Bzl = Benzyl, Anis = *p*-Anisyl.

* As the difference of the "affinity requirement" between two benzyl groups and hydrogen atom plus phenyl (or methyl) group is not known, we can say nothing about the products of the rearrangement in these cases.

Literatures.

- McKenzie and Richardson, *J. Chem. Soc.*, **123** (1923), 79; McKenzie and Wills, *ibid.*, **127** (1925), 283.
- McKenzie and Richardson, *loc. cit.*; McKenzie and Roger, *ibid.*, **125** (1924), 844.
- McKenzie and Roger, *ibid.*, **1927**, 574.
- McKenzie and Dennler, *ibid.*, **125** (1924), 2105; Orékhov and Tiffeneau, *Compt. rend.*, **178** (1924), 1619.
- and 6. McKenzie and Wills, *loc. cit.*
- Bettzieche, *Z. physiol.*, **140** (1924), 273.
- Orékhov and Tiffeneau, *Compt. rend.*, **180** (1925), 70.
- Luce, *ibid.*, 145.
- and 11. Bettzieche and Ehrlich, *Z. physiol.*, **150** (1925), 197.
- McKenzie and Roger (*J. Chem. Soc.*, **1927**, 574) obtained further the corresponding glycol as a by-product

Interpretation from the Electron Theory.

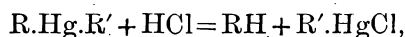
In order to deduce a more reliable theory which interprets without a provision all the rearrangements similar to pinacolone transformation, I have determined the standpoint of the interpretation in the modern electron theory which has been developed by Lapworth⁽¹⁾ and by Kermack and Robinson.⁽²⁾ This theory has great possibility to explain clearly the

(1) *J. Chem. Soc.*, **121** (1922), 461.

(2) *Ibid.*, 427.

mechanism of the most essential parts of these transformations, that is (i) elimination of water from a molecule, and (ii) migration of a group.

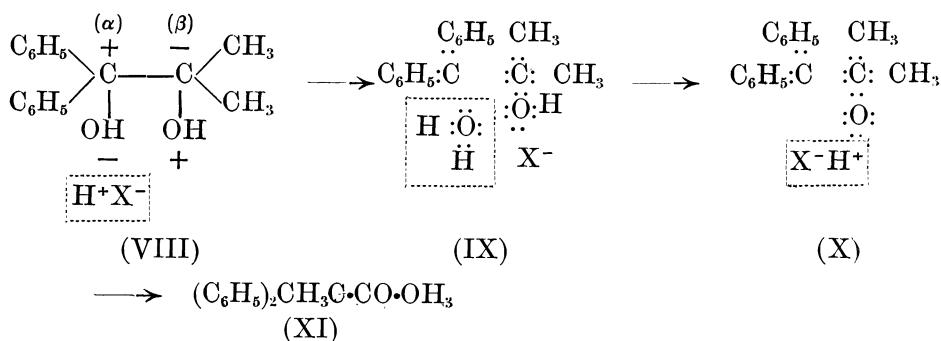
In the discussion of the mechanism of a reaction of organic compounds, especially of those which contain various hydrocarbon radicals as in our case, we must first determine the relative electro-negativity of these radicals. This question has already been solved by Kharasch and Marker,⁽¹⁾ from the studies of the reaction between unsymmetrical dialkylmercuric compounds and hydrogen chloride. The reaction runs as follows:



where the relatively electro-negative radical combines with hydrogen atom. In this way the electro-negativity of hydrocarbon radicals are found to be $\alpha-C_{10}H_7- > p-CH_3O \cdot C_6H_4- > o, p-CH_3 \cdot C_6H_4- > C_6H_5- > CH_3- > C_2H_5-$, $C_3H_7- > C_6H_5 \cdot CH_2-$ ⁽²⁾

1. **The Mechanism of Pinacolone Rearrangement.** From the fact that the pinacolone rearrangement occurs only in the presence of acid and that pinacone remains unchanged when boiled with soda-solution or when heated with water at 120°–130°, it may be assumed that *acid behaves in this case not only as dehydrating agent but also as a catalyst* as in the case of the rearrangement of phenyl-chlor-amine into *p*-chlor-aniline ($C_6H_5 \cdot NH \cdot Cl \rightarrow Cl \cdot C_6H_4 \cdot NH_2$). This assumption may be considered probable since the rearrangement of tertiary amino-alcohols occurs in the presence of nitrous acid only, without ordinary dehydrating agent.

Then the mechanism of the rearrangement of unsym. diphenyl-pinacone may be formulated as follows:



As α - and β -carbon atoms are induced respectively positive and negative, the former by the influence of phenyl and the latter by methyl group; the

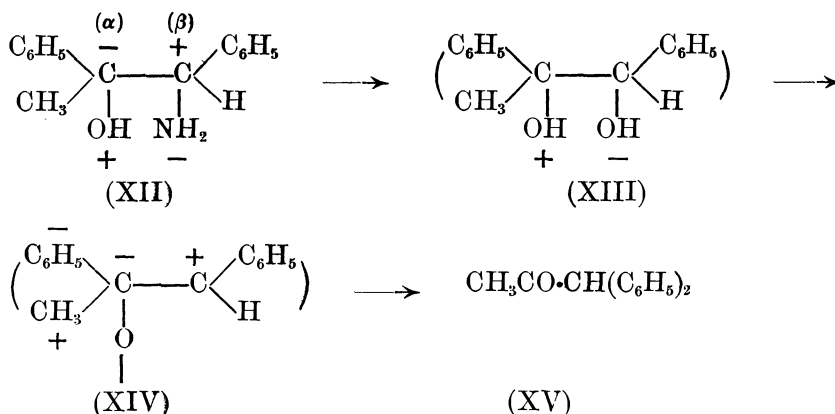
(1) *J. Am. Chem. Soc.*, **48** (1926), 3130.

(2) This result shows a good agreement with the order of "affinity requirement" given above. But this concordance is not merely accidental, as the electron theory involves in itself the principle of "affinity requirement."

theory of induced alternate polarity demands that hydroxyl group attached to α -carbon atom has negative polarity (VIII). Consequently it is this hydroxyl group that is attracted by hydrogen ion of the acid, when an acid H^+X^- is acted on this pinacone. This attraction weakens the linkage between this hydroxyl group and α -carbon atom and increases the positive character of this carbon atom. In other words, the octet around this carbon atom becomes more and more unstable, and this causes, on the other hand, the increase of the stability of the octet of the adjacent carbon atom (β) (IX). As the results of this, hydrogen atom of the hydroxyl group bound to this negative carbon atom (β) will be brought into very free state and can combine with anion X^- of the acid (X). Then the disturbance of the distribution of electrons is restored by the migration of one of the methyl groups to α -carbon atom and by sharing four electrons between β -carbon- and oxygen atoms (XI). This final product is the same as that derived by Meerwein from the theory of "affinity requirement." The rearrangement of pinacones, $R_2C(OH).CR'_2(OH)$, where R and R' are alkyl or aryl radicals, can be likewise interpreted. When the polarity difference between the two carbon atoms (α and β) is not marked, as is in the cases of pinacones with different R and R', the homologous aliphatic radicals, the rearrangement takes its course in two directions, giving two isomeric ketones in different quantities, where the proportion of the two ketones formed is dependent on the polarity difference between the α - and β -carbon atoms.

2. The Mechanism of Semipinacolinic Deamination of Tertiary Amimo-alcohols. Now taking again β -amino- $\alpha\beta$ -diphenyl- α -methyl-ethyl alcohol as an example, the "key atom" which causes the polarity in this molecule, when placed in an activated state, may be assumed to be the most negative and reactive amino group. In consequence of the induced alternate polarity caused by this negative key atom, β -carbon atom is induced strongly positive, α -carbon atom negative and the hydroxyl group positive in its turn (XII). Then the corresponding glycol, which is assumed to be formed when amino-alcohol is treated with nitrous acid, will have strongly negative hydroxyl group bound to β -carbon atom (XIII), therefore, according to the mechanism described in the last section, it must give such a "fraction of molecule" as (XIV). Further, if one of the group attached to α -carbon atom migrates to β -carbon atom in order to restore the disturbance of the affinity, the group that wanders must be the one that is more negative, since β -carbon atom has positive polarity. Thus in this case it is the phenyl group that wanders, and the final product must be diphenyl acetone (XV). This interpretation is proved by the actual product of the rearrangement.

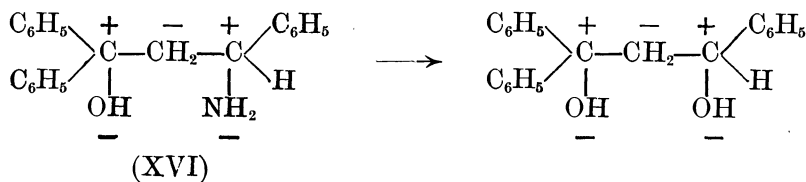
(1) Vorländer, *Ber.*, 30 (1897), 2766.

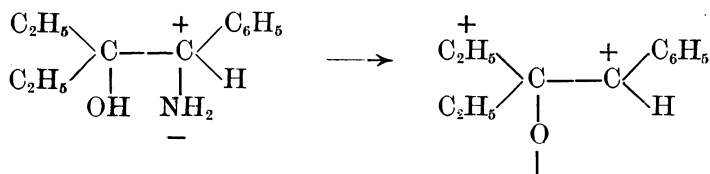


It is obvious from Table 1 that this interpretation in the prediction of the product of the semipinacolinic deamination is not only applicable in this one example, but also gives satisfactory results in many other cases. Out of a dozen examples the case which stands against this interpretation is only one, that is, that of β -amino- α - β -diphenyl- α -naphthyl-ethyl alcohol (No. 4 in the Table) in which phenyl group which is more positive than naphthyl group wanders to β -carbon atom. This might be considered due to some steric influence of the phenyl group attached to β -carbon atom, since in the case of the β -amino- α -phenyl- α -naphthyl-ethyl alcohol (No. 9) the rearrangement takes the normal course.

3. Behaviour of Tertiary Amino-Alcohols towards Nitrous Acid.

The electronic interpretation can explain why tertiary amino-alcohols generally undergo semipinacolinic deamination by nitrous acid, whereas in few cases normal displacement of amino group takes place. In the former, the state of marked polarity developed in the molecule due to the presence of a strongly negative group such as amino radical may be sufficient to cause the molecular transformation by mere catalytic action of the acid present. This may account at the same time, for the normal displacement of amino group in the cases of γ -amino- $\alpha\alpha\gamma$ -triphenyl-propyl alcohol (XVI) and of β -amino- β -phenyl- $\alpha\alpha$ -diethyl-ethyl alcohol (XVII). Because in the former, the fact that two hydroxyl groups in the corresponding glycol are induced in the same sense, may be considered to play an important rôle, and in the latter, the ethyl group cannot easily migrate to the positively polarised β -carbon atom in consequence of its positive character.





(XVII)

4. The Rearrangements of Trisubstituted α -Glycols. Which afford an interesting problem by the variety of their modes of transformation, will be discussed in another paper.

Conclusion.

Hitherto the rearrangements of pinacones and their closely related compounds have been interpreted from the theory of "affinity requirement." But as this theory is compelled to admit the provision that the migrational aptitude of a certain group is not necessarily concordant with its "affinity requirement," it cannot generally foretell the rearrangement product.

An interpretation based on the theory of induced alternate polarity and on the assumption that acid behaves in these rearrangements not only as dehydrating agent but also as a catalyst, has following advantages :

(1) The products of rearrangements of pinacones and tertiary amino-alcohols are reliably predicted by one and the same reasoning.

(2) We can also explain why tertiary amino-alcohols generally behave abnormally toward nitrous acid, whereas in certain cases normal displacement of amino group takes place.

Of course, this electronic interpretation is by no means perfect, on the contrary, there remains a fundamental problem undissolved. That is a question of the steric influence. The steric influence is an important, but an unknown factor, which, as well as the general and alternate effects due to a key atom, has a directive influence on a chemical reaction. It must be the most important task given on the electron theory to bring the nature of this influence to light. Besides this fundamental problem, the above electronic interpretation has some contradictory facts :

(1) The rearrangements of alkyl-trimethyl pinacones propose a strong objection to this interpretation, for they give ketones, $\text{CH}_3\cdot\text{CO}\cdot\text{CR}(\text{CH}_3)_2$, by the migration of the more positive group.⁽¹⁾

(2) When β -amino- β -phenyl- $\alpha\alpha$ -diethyl-ethyl alcohol is treated with nitrous acid, the main product is the corresponding glycol, as already

(1) $\text{R}=\text{C}_2\text{H}_5$, Meerwein, *Ann.*, **396** (1896), 255; $\text{R}=\text{n- and iso-C}_3\text{H}_7$, Locquin and Leers, *Bull. Soc. chim.*, **39** (1926), 426.

described, while according to the above explanation in the case of β -amino- β -phenyl- $\alpha\alpha$ -dibenzyl-ethyl alcohol the normal displacement of amino group should take place at least as easily as in the former case, since as benzyl is more positive than ethyl, it should migrate more difficultly to positively polarized β -carbon atom. But the actual products betray this prediction, for it gives the glycol only as a by-product.⁽¹⁾

These contradictions will be discussed again when a sufficient number of new experimental materials are obtained.

I wish to express my hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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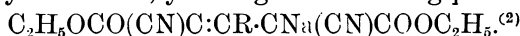
(1) McKenzie and Roger, *J. Chem. Soc.*, 1927, 574.

SYNTHESIS OF THE ESTERS OF β -BENZYL-
 α,γ -DICYANOGLUTACONIC ACID.

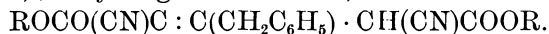
By Yoshiyuki URUSHIBARA.

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The formation of the sodium derivative of diethyl β -methyl- α,γ -dicyano-glutaconate $C_2H_5OCO(CN)C:C(CH_3) \cdot CNa(CN)COOC_2H_5$ in the condensation of ethyl ethoxy-ethylidene-cyanoacetate $C_2H_5OC(CH_3):C(CN)COOC_2H_5$ with ethyl sodio-cyanoacetate $CHNa(CN)COOC_2H_5$ let the author suppose that any compound with the general formula $C_2H_5OCR : C(CN)COOC_2H_5$ will condense with ethyl sodio-cyanoacetate, yielding the following product :



Subsequently the author carried out experiments on the synthesis of the esters of β -benzyl- α,γ -dicyanoglutaconic acid,



Diethyl β -Benzyl- α,γ -dicyanoglutaconate. The sodium derivative of this ester, $C_2H_5OCO(CN)C : C(CH_2C_6H_5) \cdot CNa(CN)COOC_2H_5$, must be given by the condensation of ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate $C_2H_5OC(CH_2C_6H_5):C(CN)COOC_2H_5$ and ethyl sodio-cyanoacetate. Ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate has been already obtained by Smith and

(2) See p. 102 and 261 of this volume.

Thorpe.⁽¹⁾ It seems difficult to obtain a sufficient amount of this compound in the pure crystalline state, for these authors describe that the ethylation product of the silver derivative of ethyl α -cyano- γ -phenyl-acetoacetate was a mixture of two isomerides, ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate and ethyl α -cyano- α -ethyl- γ -phenyl-acetoacetate, which could not be separated by distillation. The present author gave up the idea to obtain the pure ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate, and used it without separating from its isomeride.

The method of preparation of ethyl α -cyano- γ -phenyl-acetoacetate was improved as follows: Powdered sodium (2 atoms) was covered with a large amount of pure benzene and an excess of ethyl cyanoacetate (over 2 mols) was introduced gradually. On several hours' standing, the mixture was converted into a white thick paste. Phenacetyl chloride (1 mol) was then added in small portions under constant stirring and cooling. The mixture was heated on the water bath for a while, and cooled. The sodium derivative of ethyl α -cyano- γ -phenyl-acetoacetate formed in this way was extracted with water. The aqueous solution was acidified with dilute sulphuric acid and the oily substance was extracted with ether. After dehydrating the ethereal solution with calcium chloride and evaporating away the ether, the ester was distilled under diminished pressure. Ethyl α -cyano- γ -phenyl-acetoacetate was transformed into the silver derivative by dissolving it in an aqueous solution of the calculated amount of sodium hydroxide and adding to this solution the calculated amount of a silver nitrate solution. The silver compound was washed with water and completely dried in vacuum in a dark place.

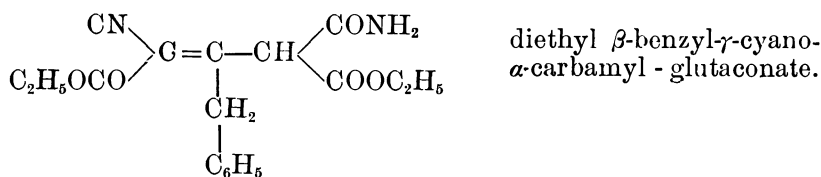
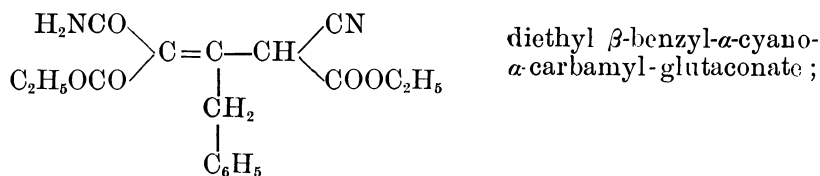
A mixture of the dried silver compound, an excess of ethyl iodide, and absolute alcohol, was boiled for a while with a reflux condenser. The alcoholic solution was filtered from silver iodide and evaporated. The residue was dissolved in ether and the ethereal solution was shaken with an aqueous solution of sodium carbonate until the latter remained alkaline. Then it was washed with water, dried with calcium chloride and evaporated. The ether was removed in vacuum over sulphuric acid as much as possible. The oily substance obtained in this way and containing ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate was used for the condensation without further treatments.

Sodium (1 gram atom) was dissolved in absolute ethyl alcohol and ethyl cyanoacetate (1 mol) was added. Then ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate (1 mol) was introduced, the above-described oily substance being assumed to consist of this compound alone. The alcoholic solution was evaporated to dryness in vacuum, and the residue was dissolved in water.

(1) *J. Chem. Soc.*, 91 (1907), 1905.

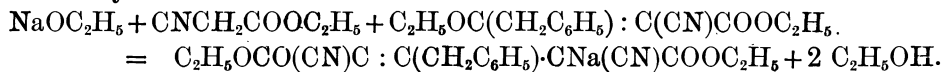
The insoluble oily substance might be the ethyl α -cyano- α -ethyl- γ -phenyl-acetoacetate which was indifferent in the reaction. This was removed by shaking the aqueous solution with ether. On adding dilute hydrochloric acid to the aqueous solution an oily substance separated out, which was extracted with ether. Some amount of the sodium derivative of ethyl cyanoacetate might be left intact, for the ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate had contained its isomeride indifferent in the reaction. On dissolving the condensation product in water, the ethyl sodio-cyanoacetate is at once transformed into sodium cyanoacetate and alcohol. Therefore, on acidifying the aqueous solution the ethyl cyanoacetate was not to be regenerated, and this fact facilitated the subsequent treatment.

The ethereal solution was washed with water. After a while, colourless crystals began to separate from the ethereal solution not yet dried. When the increase of the crystals ceased, they were collected, washed with ether and then with water. This crystalline substance was recrystallised from alcohol. It melted at 131° . By analysis it was found to be diethyl β -benzyl-cyano-carbamyl-glutaconate, and not the diethyl β -benzyl- α,γ -dicyanoglutaconate. 0.1943, 0.2022 Gr. of the substance gave 0.4465, 0.4622 gr. of CO_2 and 0.1001, 0.1044 gr. of H_2O respectively: 0.2462, 0.2727 gr. of the substance gave 18.3 c.c. (26.5° , 759.5 mm.), 20.15 c.c. (26.5° , 761.9 mm.) of nitrogen respectively. (Found: C=62.69, 62.36; H=5.77, 5.78; N=8.18, 8.15. $\text{C}_{18}\text{H}_{20}\text{O}_5\text{N}_2$ requires C=62.75; H=5.86; N=8.14%.) On heating at about 90° or dehydrating in vacuum, it lost no water. This compound must be either of the following:



The oily substance which was afterwards changed in the crystalline monohydrate must be diethyl β -benzyl- α,γ -dicyanoglutaconate, $\text{C}_2\text{H}_5\text{OCO}(\text{CN})\text{C} : \text{C}(\text{CH}_2\text{C}_6\text{H}_5) \cdot \text{CH}(\text{CN})\text{COOC}_2\text{H}_5$. In spite of the impureness

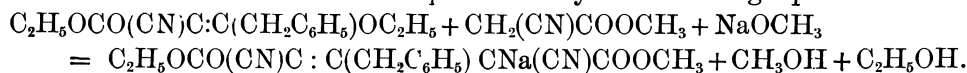
of the ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate the condensation proceeded successfully as follows :



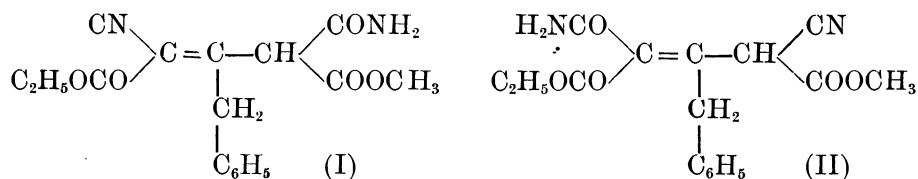
Although the sodium compound was not isolated, it was contained in the aqueous solution of the condensation product and it gave the free cyano-ester on acidifying, and the latter was then transformed into the monohydrate in the ethereal solution.

Methyl Ethyl Esters. Following the similar procedure the author carried out the experiment on the condensation of ethyl α -cyano- β -ethoxy- γ -phenyl-crotonate with methyl cyanoacetate in the presence of sodium methylate. The final product was the monohydrate of methyl ethyl β -benzyl- α , γ -dicyanoglutaconate melting at about 115° . 0.1930 Gr. of the substance gave 0.4351 gr. of CO_2 and 0.0946 gr. of H_2O ; 0.2547 gr. of the substance gave 19.3c.c. of nitrogen at 22.5° , 761.8 mm. (Found: C=61.50; H=5.49; N=8.54. $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_2$ requires C=61.79; H=5.50; N=8.48 %.) (Specimen A)

The condensation must be represented by the following equation :



The monohydrate $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_2$, in which the sodium atom is replaced by hydrogen and either of the two cyano-groups is hydrated into a carbamyl-group, must be represented by either of the following formulas :

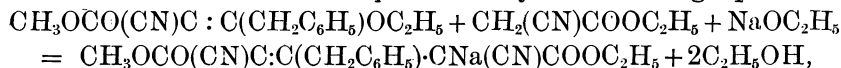


By starting from methyl α -cyano- β -ethoxy- γ -phenyl-crotonate⁽¹⁾, ethyl cyanoacetate, and sodium ethylate, another specimen of methyl ethyl β -benzyl-cyano-carbamyl-glutaconate was obtained. It melted at about 115° .

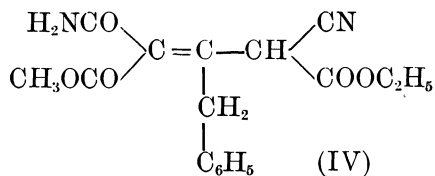
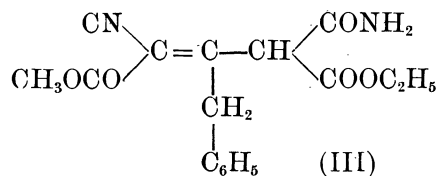
(1) This compound was prepared by a similar method as the ethyl ester. The sodium derivative of methyl cyanoacetate formed in benzene covered so compactly the surface of sodium grains that the transformation of methyl cyanoacetate into its sodium derivative was completed only by using a large excess of powdered sodium (about twice as much as necessary) and rubbing mechanically the sodium grains. On adding phenacetyl chloride and standing over night the metallic sodium disappeared. Then the mixture was worked on similarly as in the case of the ethyl ester. Methyl α -cyano- γ -phenyl-acetoacetate is a crystalline substance. This ester was transformed into methyl α -cyano- β -ethoxy- γ -phenyl-crotonate, which was used also without separating from its possible isomeride.

0.1889 Gr. of the substance gave 0.4261 gr. of CO_2 and 0.0928 gr. of H_2O ; 0.2501 gr. of the substance gave 18.9 c.c. of nitrogen at 23° , 760.7 mm. (Found: $\text{C}=61.54$; $\text{H}=5.50$; $\text{N}=8.48$. $\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_2$ requires $\text{C}=61.79$; $\text{H}=5.50$; $\text{N}=8.48\%$.) (Specimen B)

The condensation must be represented by the following equation:



and the monohydrate by either of the following:



The four formulas, (I), (II), (III), and (IV), are different from one another, and, therefore, the two specimens, A and B, must be different; but according to the example of the β -methyl compounds⁽¹⁾, they may be expected to be identical. Really the mixture of the two specimens showed no depression of the melting point, but both the pure specimens and the mixture did not melt sharply. Each of the specimens A and B is not the direct product of the condensation but the compound derived from it by a secondary change which can admit two formulas for it, for instance, (I) and (II). These specimens must be, therefore, examined in their purity. Besides, the greatest care must be exercised with regards to the identification of them, because, if they are not identical, they have a great resemblance in the constitutions. For the present the author will reserve the conclusion that the specimens A and B are identical.

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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(1) See p. 261 of this volume.