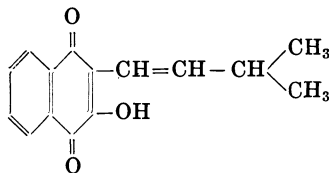


ON THE CHEMICAL CONSTITUTION OF MANGOSTIN. I.

By Seishi YAMASHIRO

Received October 7th, 1931. Published January 28th, 1932.

In the previous studies on mangostin, a yellow colouring matter extracted from the fruit-rind of *Garcinia mangostana*, many molecular formulas and various melting points were given to mangostin. W. Schmid,⁽¹⁾ P.R. Liechti,⁽²⁾ Nijdam⁽³⁾ and J. Dekker⁽⁴⁾ presented $C_{40}H_{44}O_{10}$ (m.p. $190^{\circ}C.$), $C_{20}H_{22}O_5$ (m.p. $173^{\circ}C.$), $C_{28}H_{24}O_6$ (m.p. $176.5^{\circ}C.$) and $C_{16}H_{16}O_4$ (m.p. $176.5-177^{\circ}C.$) respectively. According to the results of the recent research reported by Dekker (loc. cit.) mangostin has one methoxyl and one hydroxyl groups in a molecule. In support of this fact he has shown that the methoxyl content of mangostin is about 8% (calculated value for $C_{15}H_{13}O_3 \cdot OCH_3$ is 11.4%) and that the methylation of mangostin gives a methylmangostin, which produces an acethyl-methylmangostin on acetylation. He also perceived smells resembling those of amyl alcohol and valerianic acid on alkali-fusion of mangostin, and has come to the conclusion that mangostin may probably be a methoxyl derivative of lapachol which has the annexed formula.



The present author re-examined the experiments carried out by the above mentioned investigators, especially by Dekker, and discovered some other new constituents and properties of mangostin, those of which are intended for a communication. It has, however, to be noted here that the experiments described in this paper had been made in 1927, when the publication of them was suspended by some reason, and that they are now communicated without any corrections to the author's opinion of that time, in spite of the fact that striking progress has lately been made in the investigations of mangostin.

-
- (1) Schmid, *Ann. Chem. Pharm.* **93** (1855), 83.
 - (2) Liechti, *Arch. Pharm.*, **229** (1891), 426.
 - (3) *Rec. Trav. Chim. Pays-Bas*, **35** (1916), 346.
 - (4) Dekker, *Rec. Trav. Chim. Pays-Bas*, **43** (1924), 727.

Mangostin, which the author extracted from the fruit-rind of *Garcinia mangostana* with ethyl alcohol and purified by recrystallisation from benzene and then from dilute ethyl alcohol, is a yellow leaflet crystal, which gives a dark green coloration with ferric chloride in dilute alcoholic solution and melts at 176.5–177°C. The results of the elementary analyses and the molecular weight determinations of mangostin correspond to the formula $C_{20}H_{22}O_5$, but the results of the determinations of methoxyl group give an appreciably lower value ($OCH_3=7.50\%$) than the calculated value ($OCH_3=9.07\%$) for $C_{19}H_{19}O_4 \cdot OCH_3$.

On methylation with dimethylsulphate and potassium hydroxide in methyl alcoholic solution mangostin gives two kinds of methyl derivatives, both of which are not soluble in dilute alkalies and give the same coloration as that of mangostin with ferric chloride, and also the results of the elementary analyses and the molecular weight determinations of the derivatives correspond almost equally to a monomethyl-mangostin, $C_{19}H_{18}O_3 (OCH_3)_2$. But one is a yellowish-white needle crystal (m.p. 120.5–121°C., $OCH_3=ca. 14\%$), which corresponds to the methylmangostin (m.p. 122.5–123°C., $OCH_3=ca. 17\%$) prepared by Dekker, while the other (X) is a pale yellow leaflet crystal (m.p. 171–171.5°C., $OCH_3=10.8\%$). The compound X seems to be an intermediate product of methylmangostin, since the methoxyl content of the former, as will be seen, lies between those of the latter and mangostin and also the compound X converts into the methylmangostin by further methylation with dimethylsulphate and potassium hydroxide.

An acethyl-methylmangostin prepared by acetylation of the methylmangostin with acetic anhydride and sodium acetate crystallises from benzene into white needles (m.p. 191–191.5°C.) and gives no coloration with ferric chloride in alcoholic solution. It corresponds to the acethyl-methylmangostin (m.p. 196°C.) prepared by Dekker, but the results of the analyses and the acethyl determinations correspond to the formula $C_{20}H_{20}O_4 (OCH_3) COCH_3$.

Although the acetylation and the benzylation of mangostin were tried under various conditions and many attempts were made on the separations of reaction products, it was difficult to fractionate the reaction products into pure components. It was, however, accomplished to isolate a compound which corresponds nearly to diacethyl-mangostin.

The methylmangostin seems to be an unsaturated compound, since it easily absorbs bromine in chloroform solution. A brominated methylmangostin prepared by the action of an equimolecular quantity of bromine on the methylmangostin in dry benzene solution is a deep yellow crystalline substance (decomp.p. 160°C.) and has a composition which corresponds almost nearly to a tribromo-methylmangostin. It is, however, so unstable

to water and light that the instability renders the purification of the bromo compound a matter of difficulty, namely, the tribromo-methylmangostin converts instantaneously on contact with water into a reddish-purple viscous matter which on exposure to light passes gradually into a yellow crystalline substance. Consequently it must be recrystallised from dry benzene and kept from moisture and light.

Considering the molecular formula of mangostin as $C_{20}H_{22}O_5 = C_{19}H_{17}O_2(OH)_2-OCH_3$ from the above experimental results (notwithstanding the low methoxyl content which corresponds rather to $C_{24}H_{26}O_6$ than to $C_{20}H_{22}O_5$), the combined states of two atoms of oxygen are still unknown. To make clear it the author attempted to cause for mangostin the characteristic reactions of flavonol and also to prove the presence of some carbonyl groups in the molecule of mangostin by preparation of oxime and reduced acetylation of mangostin. He failed, however, to give any positive results.

When mangostin is subjected to alkali-fusion many decomposition products are formed. A vapour distilled from the melt during the fusion has an odour resembling that of amyl alcohol, as shown by Dekker, and condenses on cooling to a minute quantity of yellow oil. From the melt six compounds can be isolated, of which oxalic, acetic, isovalerianic acids and phloroglucinol have been identified, while the other two compounds remain undetermined. One of the two unknown compounds, however, is a sparingly water-soluble acid which crystallises from water into yellowish-white microscopic needles (m.p. $373^{\circ}C.$) and the other is a water-insoluble yellow phenolic substance (m.p. $212^{\circ}C.$), which bears resemblance to mangostin in its chemical properties, namely, it gives a dark green coloration with ferric chloride and produces on alkali-fusion isovalerianic acid, phloroglucinol, and a vapour resembling amyl alcohol. This phenolic substance, however, differs from mangostin in crystalline form, melting point and composition, having the formula $C_{16}H_{16}O_5$. By the alkali-fusion of mangostin the present author obtained no benzoic acid reported by J. R. Hill⁽¹⁾.

Summary.

Judging from the above experimental results mangostin has the molecular formula $C_{20}H_{22}O_5$ and contains one methoxyl and two hydroxyl groups. It seems to be an unsaturated compound. The formations of isovalerianic acid and the oily matter resembling amyl alcohol by the alkali-fusion of mangostin suggest the presence of a branched side chain in the molecule of mangostin, and the isolation of phloroglucinol from the melt restricts the

(1) Hill, *J. Chem. Soc.*, **107** (1915), 595.

relative positions of methoxyl group, hydroxyl groups and oxygen atoms in the molecule of mangostin.

Although the author has failed to give any positive results in the researches for the characteristic reactions of flavonol and for the presence of carbonyl group in the molecule of mangostin, he has come to the conclusion that the chemical constitution of mangostin as a methoxyl derivative of lapachol is obviously untenable, since it is impossible to yield phloroglucinol from the derivative.

Experimental Part.

Mangostin. The dry powdered fruit-rinds of *Garcinia mangostana* were extracted with alcohol, and from the extracts alcohol was distilled off. The residues were extracted with hot water to remove a reddish-brown viscous matter and after drying were recrystallised from benzene. The yield of the crude mangostin was about 4.3% of the dry rind. The raw product was recrystallised repeatedly from benzene and 60% alcohol. The pure mangostin crystallised from dilute alcohol into yellow plates and melted at 176.5–177°C.

Anal. Subst. = 0.1605; CO_2 = 0.4105; H_2O = 0.0926 gr. Found: C = 69.75; H = 6.46%.

Mol. weight, measured cryoscopically in nitrobenzene, and after Rast. Subst. = 0.0756; nitrobenzene = 14.2390 gr.; f.p. depress. = 0.110°C. Found: mol. weight = 338. Subst. = 0.00135; camphor = 0.01168 gr.; m.p. depress. = 13.5°C. Found: mol. weight = 343.

Methoxyl, measured after Zeisel. Subst. = 0.00442; AgI = 0.00251 gr. Found: OCH_3 = 7.50%.

Calc. for $\text{C}_{19}\text{H}_{19}\text{O}_4\cdot\text{OCH}_3$: C = 70.17; H = 6.43; OCH_3 = 9.07%; mol. weight = 342, and for $\text{C}_{23}\text{H}_{23}\text{O}_5\cdot\text{OCH}_3$: C = 70.22; H = 6.39; OCH_3 = 7.55%; mol. weight = 410.

It was insoluble in water, petroleum ether, carbon tetrachloride and carbon bisulphide, but soluble easily in ether, alcohol, acetone, chloroform, nitrobenzene and acetic acid. It was also soluble in dilute alkalies and gave a dark green coloration with ferric chloride in alcoholic solution.

Methylmangostin. A solution of 10 gr. of mangostin in 300 c.c. of methyl alcohol was shaken with 50 gr. of dimethyl sulphate and then with an excess of 50% potassium hydroxide solution, separating out methylmangostin as a pale yellow crystalline substance. The methylmangostin was filtered after a short standing and washed with water and recrystallised from ethyl alcohol. It crystallised into pale yellow needles from alcohol and melted at 120.5–121°C. The yield was about 7 gr.

Anal. Subst. = 0.1334; CO_2 = 0.3470; H_2O = 0.0831 gr. Found: C = 70.94; H = 6.81%.

Methoxyl, measured after Zeisel. Subst. = 0.00443; AgI = 0.00474 gr. Found: OCH_3 = 14.13%.

Calc. for $\text{C}_{19}\text{H}_{18}\text{O}_3(\text{OCH}_3)_2$: C = 70.80; H = 6.74; OCH_3 = 17.42% and for $\text{C}_{23}\text{H}_{22}\text{O}_4(\text{OCH}_3)$: C = 70.75; H = 6.60; OCH_3 = 14.60%.

It was insoluble in water and sparingly soluble in cold alcohol, but very soluble in ether, acetone, benzene and ligroine. It gave a dark green coloration with ferric chloride in alcoholic solution.

The methyl alcoholic solution filtered from methylmangostin was evaporated and acidified with dilute hydrochloric acid, separating out a yellow mass. The separated mass was filtered and recrystallised from ethyl alcohol, crystallising in pale yellow plates which melted at $171-171.5^\circ\text{C}$. The yield was about 2 gr.

Anal. Subst. = 0.1346; CO_2 = 0.3493; H_2O = 0.0806 gr. Found: C = 70.77; H = 6.70%.

Mol. weight, measured after Rast. Subst. = 0.00088; camphor = 0.00903 gr. m.p. depress. = 11.0. Found: mol. weight = 354.

Methoxyl, measured after Zeisel. Subst. = 0.00435; AgI = 0.00358 gr. Found: OCH_3 = 10.86%.

Calc. for $\text{C}_{19}\text{H}_{18}\text{O}_3(\text{OCH}_3)_2$: C = 70.80; H = 6.74; OCH_3 = 17.42%; mol. weight = 356.

This compound (X) gave the same coloration as those of methylmangostin and mangostin with ferric chloride, but it was generally less soluble in the ordinary organic solvents than the last two compounds, i.e. sparingly soluble in ether, benzene, chloroform and acetic acid in the cold state. It was also insoluble in dilute alkalies and lowered its melting point exceedingly when mixed with mangostin.

The yield of methylmangostin in proportion to that of the compound X increased with the quantity of dimethyl sulphate employed, and indeed the compound X was converted into methylmangostin on further methylation with dimethyl sulphate and potassium hydroxide.

Acethyl-methylmangostin. Two gr. of methylmangostin was mixed with 4 gr. of anhydrous sodium acetate and 20 gr. of acetic anhydride and heated for 2 hours. On cooling the reaction mixture acethyl-methylmangostin separated out as a white mass, which was filtered and washed with hot water and recrystallised from benzene, yielding white needle crystals; m.p. $191-191.5^\circ\text{C}$. The yield was about 2 gr.

Anal. Subst. = 0.1371; CO_2 = 0.3512; H_2O = 0.0831 gr. Found: C = 69.86; H = 6.78%. Acethyl. Subst. = 0.5000 gr. equivalent KOH (0.0729N.) = 16.3 c. c. Found: COCH_3 = 10.20%. Calc. for $\text{C}_{21}\text{H}_{20}\text{O}_5\cdot\text{COCH}_3$: C = 69.30; H = 6.60; COCH_3 = 10.79%.

It was insoluble in cold dilute alkalies and gave no coloration with ferric chloride in alcoholic solution.

Acethylation and Benzoylation of Mangostin. Four gr. of mangostin was mixed with 20 gr. of anhydrous sodium acetate and 60 c.c. of acetic anhydride and warmed at 40–50°C for 3 days keeping from moisture. The reaction products were extracted with ether and the ethereal solution was shaken with a solution of sodium bicarbonate to remove the acetic anhydride and then the ether was distilled off, leaving a yellow crystalline mass. The yield was about 5 gr. The raw product was fractionally recrystallised from methyl alcohol, yielding two kinds of crystals, namely, plate (m.p. 107–108°C.) and needle (m.p. 115–118°C.) crystals. The latter which was still impure was analysed.

Acethyl. Subst. = 0.5003 gr. equivalent KOH (0.0518 N.) = 41.3 c.c.
Found: COCH_3 = 18.39%. Calc. for $\text{C}_{20}\text{H}_{20}\text{O}_5(\text{COCH}_3)$: COCH_3 = 20.09%.

Mangostin was also acetylated with the addition of zinc powder, obtaining none other than the above mentioned reaction products.

Benzoylation was also carried out by the action of benzoyl chloride on mangostin in alkaline solution, but the reaction products were so complex as to render their isolations a matter of difficulty.

Tribromo-methylmangostin. In a solution of 1 gr. of methylmangostin in 10 gr. of dry benzene an equimolecular quantity of bromine was added drop by drop, precipitating a yellow crystalline substance. The precipitates were filtered and recrystallised from dry benzene, forming the aggregates of deep yellow irregular leaflet crystals. The yield was about 1 gr. It decomposed at about 160°C. When this yellow compound had come in contact with water, it converted instantaneously into a reddish-purple viscous matter, which on exposure to light changed gradually again into a yellow crystalline substance.

Anal. Subst. = 0.2041; AgBr = 0.1880 gr. Found: Br = 39.22%. Calc. for $\text{C}_{21}\text{H}_{23}\text{O}_5\cdot\text{Br}_3$: Br = 40.34%.

Alkali-fusion of Mangostin. A mixture of 300 gr. of potassium hydroxide and 50 gr. of water was heated to about 170°C. and 30 gr. of mangostin was gradually added to the fusion mixture under constant stirring. A vapour evolved from the melt during the fusion process was condensed to a yellow oil, which had an odour resembling that of amyl alcohol. When mangostin had been dissolved homogeneously, the melt was cooled and pulverized quickly and dissolved in an ice cold dilute sulphuric acid, leaving a dark brown viscous matter. The aqueous solution was filtered from the

insoluble viscous matter and subjected to steam distillation. Volatile acids were separated from the distillates and fractionated by distillation into two parts. One of the fractions boiled at 117–119°C.; yield ca. 4 gr. It was converted into an anilide by heating with aniline. The anilide melted at 114°C. and was identified with acetanilide. The other fraction boiled at 177–180°C.; yield ca. 4 gr. It was neutralized with ammonium carbonate and heated to 230°C. in a sealed tube, yielding an amide which melted at 135°C. and was identified with isovaleramide.

The aqueous solution from which the volatile acids had been distilled off was extracted with ether. The ethereal solution was washed with a solution of sodium bicarbonate and distilled down to dryness, and the phenolic residue was recrystallised from water, yielding white plate crystals; yield ca. 1.2 gr. It melted at 215°C. in the anhydrous state.

Crystalline water. Air dried subst. = 0.1450; after drying at 120° = 0.1126 gr. Found: H_2O = 22.34%. Calc. for $\text{C}_6\text{H}_6\text{O}_3 \cdot 2\text{H}_2\text{O}$: H_2O = 22.22%.

Anal. Subst. = 0.1676; CO_2 = 0.3586; H_2O = 0.0747 gr. Found: C = 58.36; H = 5.00%. Calc. for $\text{C}_6\text{H}_6\text{O}_3$: C = 58.43; H = 4.92%.

It produced no precipitates with lead acetate in an aqueous solution and gave bluish-violet coloration with potassium hydroxide and hydrogen peroxide. Phloroglucinol-test with pine tree and concentrated hydrochloric acid was positive and also no depressions in the melting point of the phenolic product were observed when it was mixed with phloroglucinol.

The aqueous solution from which the phenolic part was extracted was concentrated and extracted again with ether, isolating only oxalic acid; yield ca. 1.5 gr.

The dark brown viscous matter separated from the acidic solution of the melt was dried and recrystallised from benzene, forming yellow needle crystals. The yield was about 18 gr. It resembled closely to mangostin in its chemical properties, namely, solubilities in organic solvents, coloration with ferric chloride, and the productions of isovalerianic acid, phloroglucinol, and of a vapour resembling amyl alcohol on alkali-fusion. It, however, melted at 212°C. and lowered its melting point remarkably when mixed with mangostin.

Anal. Subst. = 0.1792; CO_2 = 0.4358; H_2O = 0.0863 gr. Found: C = 66.33; H = 5.40%.

Mol. weight, measured after Rast. Subst. = 0.00056; camphor = 0.00556 gr.; m.p. depress. = 14. Found: mol. weight = 288.

The benzene mother liquor was evaporated and extracted repeatedly with hot water, separating out pale yellow microscopic needle crystals on cooling. It melted at 373°C. The yield was 0.06 gr.

Anal. Subst. = 0.1506; CO_2 = 0.3328; H_2O = 0.0459 gr. Found: C = 60.27; H = 3.41%.

It was insoluble in chloroform and petroleum ether, but very soluble in ethyl alcohol, ether and acetic acid. It was acidic in alcoholic solution and dissolved in dilute alkalies, giving a strong fluorescence.

The last two compounds obtained from the brown viscous matter remain undetermined.

In conclusion, the author wishes to express his hearty thanks to Prof. Riko Majima for his kind guidance in this research.

Chemical Institute, Faculty of Science,
Tohoku Imperial University, Sendai.

A THEORY OF THE RATE OF SOLUTION OF GAS INTO LIQUID.

By Susumu MIYAMOTO.

Received October 1st, 1931. Published January 28th, 1932.

A theory of the rate of solution of gas into liquid, which may be much probable not only for the interpretation of the phenomena already studied by many writers, but also for the interpretation of the rate of oxidation of sodium sulphite solution, was described in the previous papers.⁽¹⁾ The present paper is intended to discuss the new theory in comparison with other theories.

Noyes and Whitney⁽²⁾ interpreted the rate of reaction at solid-liquid interfaces by the theory based upon the assumptions that the process is composed of two stages, namely extremely rapid reaction in the interfacial layer and slow diffusion of the reactants and resultants from the layer. Nernst⁽³⁾ extended this diffusion theory and proposed that the reaction velocity in heterogeneous systems is generally composed of two stages above described.

Adeney and Becker⁽⁴⁾ had studied the rate of solution of air, oxygen and nitrogen from the surface of bubbles of known magnitude into water, and proposed the following equation to interpret the experimental results,

(1) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 13; S. Miyamoto and A. Nakata, *ibid.*, **6** (1931), 18; S. Miyamoto, T. Kaya and A. Nakata, *ibid.*, **6** (1931), 140.

(2) *Z. physik. Chem.*, **23** (1897), 689.

(3) *Ibid.*, **47** (1904), 52.

(4) *Phil. Mag.*, **38** (1919), 317; **39** (1920), 385; **42** (1921), 87.

$$\frac{dw}{dt} = SAp - f \frac{S}{v} w, \dots\dots\dots (1)$$

where A is the initial rate of solution per unit area, f the coefficient of escape from the liquid per unit area and volume, S the area of the boundary surface, v the liquid volume, p the gas pressure and w the weight of gas dissolved.

Donnan and Masson⁽¹⁾ modified the equation of Adeney and Becker, and proposed the following equations.

$$\frac{dw}{dt} = k_2(kc_g - c_l), \dots\dots\dots (2)$$

when the system obeys Henry's law, and

$$\frac{dw}{dt} = k_2[f(c_g) - c_l], \dots\dots\dots (2')$$

when Henry's law does not hold.

In these equations, c_g is the concentration of absorbable gas in the gas phase, c_l the corresponding concentration in the liquid phase, k the Henry's law coefficient, and k_2 a constant. The above mentioned equations may be expressed by a slight rearrangement in the form,

$$\frac{dw}{dt} = k[c_\infty - c_l] \dots\dots\dots (3)$$

where c_∞ is the concentration of saturated solution, and k a constant.

For the rate of solution of gas into liquid, the following expression was proposed by Lewis, Whitman and Keats,⁽²⁾

$$\frac{dw}{dt} = k_p[p_g - p_l] \dots\dots\dots (4)$$

where p_g and p_l are the partial pressure of the absorbable component in the gas phase and in the liquid phase respectively.

Whitman and Keats⁽³⁾ assumed the existence of a stationary gas film and a stationary liquid film at the boundary surface and proposed the following equation for the rate of absorption.

(1) *J. Soc. Chem. Ind.*, **39** (1920), 236.

(2) Lewis, *J. Ind. Eng. Chem.*, **8** (1916), 825; Whitman and Keats, *ibid.*, **14** (1922), 185.

(3) *Ibid.*

$$\frac{dw}{dt} = k_p(p_1 - p_2) = k_c(c_2 - c_3) \dots \dots \dots (5)$$

where $p_1 - p_2$ is a partial pressure gradient of the solute in the gas film, and $c_2 - c_3$ is a concentration gradient in the liquid film, k_p and k_c being constants.

Davis and Crandall⁽¹⁾ assumed that the upper surface of the liquid film is almost instantaneously saturated with the gas and interpreted the results of their research on the rate of solution of oxygen into water by the equation,

$$\frac{1}{S} \left(\frac{dn}{dt} \right) = k_l(c_\infty - c_l), \dots \dots \dots (6)$$

where c_∞ is the saturation concentration of the dissolved gas, c_l the concentration of the gas in the liquid phase, k_l a constant, n the number of moles of the gas in the liquid phase, and S the area of the boundary surface.

The idea of Davis and Crandall is similar to that of Nernst, Noyes and Whitney, and the equation (6) is quite the same as the equation (3). When the gas reacts with a component in the liquid phase, the rate of absorption of the gas would depend upon the concentration of the solute. Davis and Crandall⁽²⁾ proposed the following equation for the rate of solution when the reaction velocity is very great,

$$\frac{1}{S} \left(\frac{dn}{dt} \right)_{\text{initial}} = k_l(c_\infty + c_m), \dots \dots \dots (6')$$

where c_m is the concentration of the reacting solute in the main body.

A New Theory of the Rate of Solution of Gas into Liquid.

The above mentioned theories are based upon two assumptions; the existence of a stationary film of liquid or stationary films of liquid and gas, and the instantaneous saturation of the upper layer of the stationary film with the gas. These assumptions will not be satisfied in some cases, as will be discussed in the later. The existence of stationary film of such thickness as the diffusion theory requires will be questionable, when the bulk of the liquid is well agitated with a proper stirrer, and the assumption of instantaneous saturation of the upper layer of the liquid with gas can not be adopted to interpret the rate of oxidation of sodium sulphite solution.

The theory of the present writer⁽³⁾ is based upon quite different assumptions, as will be described in the following.

(1) *J. Am. Chem. Soc.*, **52** (1930), 3757.

(2) *Ibid.*, **52** (1930), 3769.

(3) The theory, described in the previous papers, loc. cit., was slightly revised.

The process of solution of gas into liquid can be separated in two processes, namely the penetration of gas molecules into the liquid phase, and the escape of the gas molecules from the liquid phase. Then the rate of solution of gas into liquid can generally be expressed by

$$\frac{N}{S} \frac{dn}{dt} = N'' - N''', \dots\dots\dots (7)$$

where n is the number of moles of the absorbable gas, N Avogadro's constant, N'' the number of molecules of gas which enters into the liquid phase per unit area of the interface per unit of time, N''' the number of molecules of the gas which escapes the liquid phase per unit area per unit of time, and S the area of the boundary surface.

According to the kinetic theory of gases, the value N'' should be a fraction of the number of molecules which collide with the unit area of the interface per unit of time, N' , then,

$$N'' = \beta N', \dots\dots\dots (8)$$

where β represents the ratio of the number of molecules which penetrate into the liquid phase and the number of molecules which collide with the liquid phase, N' being the number of molecules which collide with the unit area of the boundary surface per unit of time.

By Maxwell's distribution law of velocities,

$$dN = \frac{N}{\sqrt{\pi}\alpha} e^{-\frac{u^2}{\alpha^2}} du, \dots\dots\dots (9)$$

where dN means the number of molecules whose components of velocities at right angles to one definite plane lies between u and $u + du$ among N molecules, and

$$\alpha^2 = \frac{2RT}{M}, \dots\dots\dots (10)$$

where R the gas constant T the absolute temperature, and M the molar weight of the gas. It is then easily seen that the value N' can be expressed by

$$N' = \int_0^\infty \frac{N}{V\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{Np}{\sqrt{2\pi MRT}}, \dots\dots\dots (11)$$

Where V is the molar volume of the gas, N Avogadro's constant, P the partial pressure of the gas, N/V being the number of molecules per unit volume of gas.

Now an assumption is proposed. Among the molecules, which collide with the liquid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0 , are able to enter into the liquid phase. Then value N'' will be expressed by

$$N'' = \int_{u_0}^{\infty} \frac{N}{V\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{Np}{\sqrt{2\pi}MRT} e^{-\frac{Mu_0^2}{2RT}} \dots\dots (12)$$

From (8), (11) and (12) it is seen that

$$\beta = e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (13)$$

From the similar assumption, that among the molecules of gas in the liquid phase, only those, which collide with the interface with the velocities whose components at right angles to the boundary surface are greater than a threshold value u'_0 , are able to escape the liquid phase, we can obtain the value N''' from the Maxwell's distribution law,

$$N''' = \int_{u'_0}^{\infty} \frac{c_l N}{1000\sqrt{\pi}\alpha} u e^{-\frac{u^2}{\alpha^2}} du = \frac{c_l N}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu'^2_0}{2RT}}, \dots\dots (14)$$

where c_l is the concentration of the gas in the liquid phase, N Avogadro's constant, $c_l N/1000$ being the number of molecules of the gas per unit volume of the liquid. The concentration of the gas in the liquid phase will depend upon the depth of the liquid, and strictly speaking, the mean value of the concentrations of the effective region should be employed for the value c_l , but when the bulk of the liquid is stirred, its concentration may be employed as a first approximation.

From the equations (7), (12) and (14) we have

$$\frac{N}{S} \frac{dn}{dt} = \frac{Np}{\sqrt{2\pi}MRT} e^{-\frac{Mu_0^2}{2RT}} - \frac{c_l N}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu'^2_0}{2RT}},$$

or

$$\frac{dn}{dt} = \frac{p}{\sqrt{2\pi}MRT} S e^{-\frac{Mu_0^2}{2RT}} - \frac{c_l}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu'^2_0}{2RT}}, \dots\dots (15)$$

This is the general equation for the rate of solution of gas into liquid, obtained from the new theory. The values of u_0 and u'_0 depend upon the nature of gas and liquid.

The initial rate of solution, or the rate of solution of gas when the liquid is perfectly free from the gas, can be obtained from the above equation by putting $c_l = 0$,

$$\left(\frac{dn}{dt}\right)_{\text{initial}} = \frac{p}{\sqrt{2\pi MRT}} S \cdot e^{-\frac{Mu_0^2}{2RT}}, \dots\dots\dots (16)$$

When the liquid is saturated with the gas, $dn/dt = 0$. Then at the state of saturation,

$$\frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} = \frac{c_\infty}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}}, \dots\dots\dots (17)$$

where c_∞ is the concentration of the saturated solution.

Then the equation (15) can be expressed in the form

$$\frac{dn}{dt} = KS(C_\infty - C_l), \dots\dots\dots (18)$$

where

$$K = \frac{1}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (19)$$

The equation (18) is quite the same as the equation (3). Thus the equation (3), experimentally obtained and theoretically explained by old theories, was also derived from the new theory.

The equations (15), (16) and (18) were derived without the assumption of the existence of stationary boundary films, and these equations will also be satisfied, when the bulk of the liquid phase is quiescent and the existence of a stationary liquid film should be taken into considerations. In this case,

$$n = n_1 + n_2 \dots\dots\dots (20)$$

where n is the total number of moles of the absorbed gas in the liquid phase, and n_1 and n_2 the number of moles of the gas in the stationary liquid film and in the bulk of liquid respectively.

$$\frac{dn}{dt} = \frac{dn_1}{dt} + \frac{dn_2}{dt} \dots\dots\dots (21)$$

Now,

$$\frac{N}{S} \frac{dn_1}{dt} = xN'' - yN''' - K(c_s - c_l) \dots\dots\dots (22)$$

where xN'' is a portion of gas molecules which enter into liquid phase per unit of area per unit of time, yN''' a portion of gas molecules which escape

the liquid phase per unit of area per unit of time, $K(c_s - c_l)$ the number of molecules of gas which enter into the bulk of liquid from the stationary film by diffusion, c_s the concentration of gas at the upper surface of the film, c_l the concentration in the bulk of liquid, N Avogadro's constant, S the area of the boundary surface, and x and y the constants less than 1.

$$\frac{N}{S} \frac{dn_2}{dt} = (1-x)N'' - (1-y)N''' + KS(c_s - c_l). \quad \dots\dots\dots (23)$$

From the equations (21), (22) and (23),

$$\frac{N}{S} \frac{dn}{dt} = N'' - N''' \quad \dots\dots\dots (24)$$

From the equations (12), (14) and (24) we have

$$\frac{dn}{dt} = \frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} - \frac{cS}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}},$$

which is the equation (15), and by a slight rearrangement,

$$\frac{dn}{dt} = KS(c_\infty - c),$$

which is the equations (18). In this case the mean value of concentrations of the effective region should be employed for the value c .

Discussion.

The rate of oxidation of sodium sulphite solution and the effect of many substances on the velocity were investigated by many writers.⁽¹⁾ The present writer has also studied the rate of oxidation of the same substance under special conditions, and from the following reason an assumption, that the rate of oxidation obtained by the present writer is equivalent to the rate of solution of oxygen into water, free from oxygen, was proposed.

(1) The rate of oxidation of sodium sulphite solution, obtained, is the maximum value, which does not increase further with the increase of concentration of sodium sulphite. It was also found that this maximum value is not a specific value of sodium sulphite solution. The maximum velocities

(1) Bigelow, *Z. physik. Chem.*, **26** (1898), 493; Titoff, *Z. physik. Chem.*, **45** (1903), 641; Bäckstrom, *J. Am. Chem. Soc.*, **49** (1927), 1465; Alyea and Bäckstrom, *J. Am. Chem. Soc.*, **51** (1929), 90.

of oxidation of sodium sulphite, stannous hydroxide and ferrous hydroxide are identical under the same conditions.⁽¹⁾

(2) The rate of oxidation of sodium sulphite solution does not increase above this maximum value with the further increase of concentration of sodium sulphite, on the contrary it decreases when the concentration is very great.⁽²⁾ The total quantity of these substances oxidized during a definite time interval in a same vessel is not greater than that when they are oxidized alone. The rate of absorption of oxygen by the solution does not increase by mixing them.⁽³⁾

(3) The maximum rate of oxidation of sodium sulphite solution is proportional to the area of the interface of the solution.⁽⁴⁾ It was also confirmed that this maximum value is proportional to the partial pressure of oxygen.⁽⁵⁾

(4) As was described in the previous paper,⁽⁶⁾ the rate of solution of oxygen, calculated from the maximum rate of oxidation of sodium sulphite solution, has nearly the same value as the initial rate of solution of oxygen into water, observed directly by several writers.

From these reasons, the maximum rate of oxidation of sodium sulphite solution is equivalent to the rate of solution of oxygen into water, free from oxygen, which is expressed by the equation (16), according to the theory of the present writer. From the equation (16), the value u_0 was calculated,⁽⁷⁾ using the maximum rate of oxidation of sodium sulphite solution, observed, and was found that the value u_0 is 1.65×10^5 cm./sec., approximately 3.4 times the root-mean-square velocity of oxygen gas and is independent of temperature in the range 15° — 35°C .

The diffusion theory assumes the existence of a stationary film at the interface. According to the new theory the equation (3) was obtained when the stationary film is not exist, as when the stationary film exists. When the liquid phase is quiescent, the existence of a stationary liquid film will be very probable, but when the liquid phase is well stirred, the assumption that a stationary liquid film of such thickness as that, calculated by Brunner⁽⁸⁾ and Crandall⁽⁹⁾ from the diffusion theory (2×10^{-2} — 2×10^{-3} cm.), exists at the interface, can not be accepted without direct confirmations.

(1) Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **3** (1928), 98; **3** (1928), 137.

(2) Miyamoto and Kaya, *ibid.*, **6** (1931).

(3) Miyamoto, this Bulletin, **2** (1927), 192; **4** (1959), 132.

(4) Miyamoto and Nakata, *ibid.*, **6** (1931), 9.

(5) Miyamoto, Kaya and Nakata, *ibid.*, **5** (1930), 229.

(6) Miyamoto and Nakata, *ibid.*, **6** (1931), 22.

(7) *Ibid.*

(8) *Z. physik. Chem.*, **47** (1904), 99.

(9) *J. Am. Chem. Soc.*, **52** (1930), 3760.

As a result of the study on the oxidation velocity of sodium sulphite solution by oxygen in the presence of molecular film of fatty acid,⁽¹⁾ it was ascertained that when the bulk of sodium sulphite solution is well agitated, the thickness of stationary film, if it exist, should be less than the length of a molecule of palmitic acid (23.7×10^{-8} cm.).

The result of the measurement of the oxidation velocity of sodium sulphite solution studied by the present writer, will be difficult to be interpreted by the diffusion theory, which requires the existence of a stationary film whose thickness is about 10^4 times the value confirmed experimentally⁽²⁾. The fact that the rate of oxidation of sodium sulphite solution is independent of the concentration of sodium sulphite in the range of about 0.3–0.7 normal, will also be difficult to be explained by the diffusion theory, according to which the interface is instantaneously saturated with gas. The equation (6')

$$\frac{1}{S} \left(\frac{dn}{dt} \right)_{\text{initial}} = k_l(c_{\infty} + c_m) ,$$

which is based upon the assumption that the upper layer of the surface film is almost instantaneously saturated with gas, does not hold in the case of the oxidation of sodium sulphite solution. The oxidation velocity is independent of the concentration in the range above described; it depends upon the concentration when the concentration is very small. According to the theory of the present writer, the rate of oxidation of sodium sulphite solution is less than the initial rate of solution of oxygen into water, when the concentration of sodium sulphite is very small, and the rate of oxidation is greater than the initial rate of solution of oxygen into water, when the concentration of sodium sulphite solution is in the range of 0.3–0.7 normal. In the former case, the rate of oxidation depends upon the concentration of sodium sulphite solution, and in the latter case, the rate of oxidation is equivalent to the initial rate of solution of oxygen into water, free from oxygen, which is expressed by the equation (16), and is independent of the concentration of sodium sulphite solution.

The rate of solution of oxygen into sodium sulphite solution decreases when the concentration of sodium sulphite solution is very great,⁽²⁾ as was above described. This fact will be explained by the equation (6'), which is based upon the diffusion theory, if the decrease of solubility of gas c_{∞} be taken into consideration, but the diffusion theory is not satisfied for the interpretation of the initial stage of the rate of oxidation of sodium sulphite solution, as was above described. According to the new theory it is easily

(1) Miyamoto, Kaya and Nakata, this Bulletin, **6** (1931), 133.

(2) Miyamoto and Kaya, this Bulletin, **6** (1931).

explained by the consideration that in this stage the rate of oxidation is also equivalent to the rate of solution of oxygen into the solution, free from oxygen, which is expressed by the equation (16), but the value u_0 , which depends upon the nature of the liquid phase, increases with the increase of the concentration of sodium sulphite solution.

The coincidence of the oxidation velocities⁽¹⁾ of sodium sulphite, stannous hydroxide and ferrous hydroxide in sodium hydroxide solution under the same conditions by air is also a favourable experimental fact to the theory of the present writer. The maximum oxidation velocity of sodium sulphite solution is proportional to the partial pressure of oxygen, as the new theory requires. The maximum oxidation velocity is equivalent to the value expressed by the equation (16).

In conclusion it can be described that the new theory interprets not only the experimental facts which are explained by the diffusion theory, but also those, which will be difficult to be explained by the old theory.

The new theory is very reasonable in the point of view that it does not assume the existence of a stationary liquid film at the interface, since the existence of a stationary liquid film of such thickness as that calculated by the diffusion theory is questionable, when the bulk of the liquid is well agitated with a stirrer.

Summary.

(1) A theory of the rate of solution of gas into liquid was proposed, which is based upon the assumptions that among the molecules of gas, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0 , can enter into the liquid phase, and that among the molecules of gas in the liquid phase, only those which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value u_0' , can escape the liquid phase.

(2) A short discussion of the theory in comparison with the old theories was described.

(3) Rate of oxidation of sodium sulphite solution, which will be difficult to be explained by the old theory, was interpreted by the new theory.

Laboratory of Physical Chemistry,
Hiroshima University, Hiroshima.

(1) Loc. cit.

THE RELATION BETWEEN KOLBE'S REACTION AND HYDROGEN ION CONCENTRATION. THE MECHANISM OF KOLBE'S REACTION.

By Hamilton Ryoichi MATSUDA.

Received October 24th, 1931. Published January 28th, 1932.

Various theories have been advanced to explain the mechanism of Kolbe's reaction, since the great Leipzigian professor discovered it in 1849. None of these theories, however, is convincing for lack of sufficient evidence. The present author has been studying the electrolyses of ammonium and potassium acetates in aqueous solution for some time. The results of his investigation have been published in the Journals of the Chemical Society of Japan in the vernacular language (51 (1930), 126; 51 (1930), 632; 52 (1931), 249; 52 (1931), 756).

During the author's examination of acetate solutions of smaller concentration, his notice was drawn to the fact that the colours of the indicator added to the electrolyte for pH determination had entirely disappeared in course of the experiments. This quite unanticipated phenomenon prompted him to take in hand a fresh investigation on the mechanism of the so-called Kolbe's reaction.

The electrolytes after having been electrolysed for some time were proved to contain certain oxidizing substances, setting iodine free from potassium iodide solution. It is now the author's purpose to determine the amounts of such oxidizing substances formed in course of the electrolyses of the two acetates, and compare them with those of ethane, which is formed simultaneously.

Experimental.

The apparatus used for electrolysis were the same as those mentioned in the preceding papers, while the conditions under which the electrolyses were carried out, throughout the present investigation, were as follows:

Current density: 10 A/dm² excepting the two cases of 0.1% NH₄Ac and 0.1% KAc, where 9 A/dm² and 5.1 A/dm² were applied respectively.

Temperature: 8–10° C., excepting the cases of electrolytes of the smallest concentrations, where the temp. was raised to 15–20° C.

Test for hydrogen peroxide: The presence of this substance was attested by means of a titanium sulphate solution.

Potassium permanganate test: 20 c.c. of the sample solution was acidified with an excess of sulphuric acid, and titrated by means of n/100 KMnO₄ solution.

Potassium iodide and starch test: 20 c.c. of the sample solution was added to KI solution, and iodine set free was titrated with $n/100$ thiosulphate solution, using a starch solution as the indicator. When reaction is thought to have ceased, a little more KI was added to ascertain its sufficiency.

Table 1.

Electrolyte		Duration of electrolysis	After electrolysis				$C_2H_6\%$ in the gas sample
composition	pH		pH	H_2O_2	$KMnO_4$	KI+starch	
NH_4Ac 0.1%	6.65	2½ min.	6.6	abs.	1 drop	no colouration	0
" 0.3	6.78	6	6.8	trace	1	trace	0
" 0.5	6.8	10	6.9	"	3	Thiosulphate 1 drop*	0.1
" 0.7	"	14	7.8	pres.	25	11	13.7
" 1.0	6.9	2	7.5	abs.	3	1	—
" "	"	20	8.2	pres.	37	1	28.0
" 3.0	7.0	30	8.3	"	61	4	28.8
" "	"	60	"	"	255	2	—
" 5.0	7.05	½	7.1	abs.	2	1	29.3
" "	"	48	8.2	pres.	130	8	—
" "	"	96	8.3	"	750	32	—

* 25 drops = 1 c.c.

From the above table we may gather interesting relations existing between ethane formation and oxidizing action of the electrolysed solutions on potassium iodide. The first two solutions in Table 1 neither evolved ethane, nor gave oxidizing substances (the details of the electrolytic gases were given in the latest paper, loc. cit.). By the 0.5% NH_4Ac solution, which comes third in the table, however, ethane was evolved for the first time, and at the same time some oxidizing substances were found to exist in the solution; like results were obtained in the rest of solutions.

With regard to the 5.0% NH_4Ac solution, the last mentioned in the table, the amount of oxidizing substances was observed gradually to increase as electrolysis went on, while, on the contrary, the quantity of ethane to become less and less. The latter fact was already referred to in the previous paper.

Again, hydrogen peroxide became detectable when electrolysis was continued for some time (in last two cases) but not immediately after its inception (as in the first case). These facts will be more fully stated in the subsequent case of potassium acetate solutions.

The consumption of $KMnO_4$ solution suggests the presence of certain reducing substances. They may be hydrogen peroxide, some other peroxide-

like substances, formaldehyde, or the like. The amount of such reducing substances was also observed to increase with the progress of electrolysis.

The following table shows the results obtained of electrolyses of potassium acetate solutions (0.1%—5.0%).

Table 2

Electrolyte		Duration of electrolysis	After electrolysis				C ₂ H ₆ % in the gas sample
composition	pH		pH	H ₂ O ₂	KMnO ₄	KI+starch	
KAc 0.1%	5.85	2 min.	5.9	abs.	0 drop	No colouration	0
„ 0.4	5.9	6.4	„	„	„	„	0.2
„ 0.5	„	8	„	„	4	trace	2.8
„ 1.0	„	15	8.2	pres.	28	Thiosulphate 7 drops	15.2
„ 5.0	6.0	1h. 15m.	8.5	„	15.5 c.c.	„ 70	27.8

The percentages of ethane evolved from 1.0 and 5.0% potassium acetate solutions were determined by analysing gas samples collected during the first 4 and 3 minutes of electrolysis respectively. In these cases of potassium acetate, the formation of ethane was observed to take place always accompanied with that of oxidizing substances, just as much as in the case of the ammonium salt.

It is also noticeable that when the concentration of the electrolyte was comparatively small, or the pH value of the solution was but slightly raised above 6 no trace of hydrogen peroxide, which seems to have an important bearing on the oxidizing substances in question, was detected. It will, therefore, be highly interesting to push on investigation along this line.

To know how the solutions of potassium acetate behave in course of electrolysis on a broader range of pH, the solutions acidified with acetic acid, or made alkaline by the addition of ammonium carbonate were investigated. The following tables and figures show the results of the electrolysis of a solution, which contained 5.0 gr. KAc and 1.4 gr. HAc per 100 c.c. Although the electrolytic gas in this case was not analyzed, it was approximately estimated by adopting the principle that the electrolytes of similar compositions give similar ethane formation curves, and that the duration of ethane formation is in proportion to the concentration of a like electrolyte, if the current of the same anodic density be applied, the said principle being derived from the results of the experiment No. 4, which treated the (20% KAc+5% HAc) solution, as was described in the first paper and the experiments Nos. 1, 5, 8, 11, 14, 17,

etc. (vid. also the third paper (loc. cit.)) Thus it may be regarded that ethane formation in the above case will reach the maximum point three quarters of an hour after the start of an electrolytic process, and is about

Table 3.

Electrolyte, (KAc 5.0 gr. + HAc 1.4 gr.) per 100 c.c.,
Original pH = 5.0, $D_A = 10 \text{ A/dm}^2$, Temp. = $8-10^\circ\text{C}$.

Duration of electrolysis	After electrolysis			
	pH	H ₂ O ₂	KMnO ₄	KI+starch
35 min.	5.5	abs.	4 drops	Thiosulphate 4 drops
45	5.9	"	"	5
50	7.3	pres.	20	16
60	7.5	"	"	19
70	8.5	"	2.3 c.c.	17
1½ hours	8.75	"	6.5	3
2	"	"	22	68
2½	8.7	"	53	9.8 c.c.
3¼	"	"	110	14.6
4	"	"	120	16.4
5	—	"	160	14.6

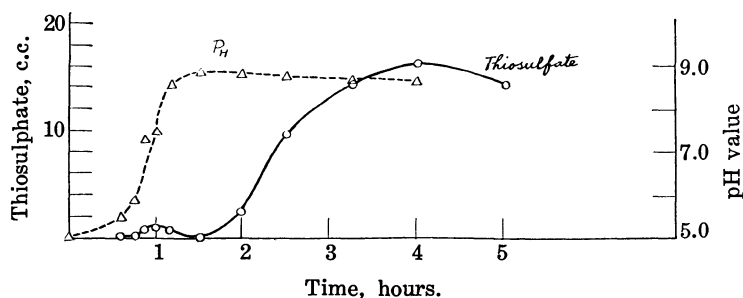
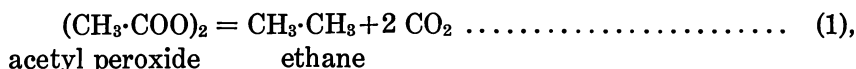


Fig. 1.

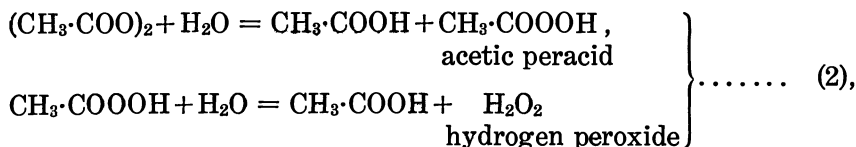
(KAc 5.0 gr. per 100 c.c.) solution, $D_A = 10 \text{ A/dm}^2$, Temp. = $8-10^\circ\text{C}$.

through in another 45 minutes. These relations lead to the conclusion that ethane formation predominates over the formation of oxidizing substances at the earlier stages of electrolysis, but vice versa at the later stages.

If we assume that acetyl peroxide is first formed at the anode, and the most of it is decomposed at the earlier stages of electrolysis according to the following equation :



and only a small portion of it remains as such, or is decomposed according to the following scheme :



the decomposition of acetyl peroxide according to the equation (1) must be regarded to decline at the later stages of electrolysis, the chemical change (2) predominating over it. It will be superfluous to say that the two acids involved in the equation (2) take the form of the corresponding salts, when the solution becomes alkaline. This assumption will go a long way to explain the fact, observed so far.

As hydrogen peroxide, which is one of the final decomposition products of acetyl peroxide, easily decomposes in alkaline solutions, its total amount can not continue to increase with the progress of electrolysis, which naturally involves the alkalinity of the solution, but must begin to decrease at a certain point. This explanation will satisfactorily account for why the thiosulphate curve in Fig. 1 falls after once passing over the maximum point. Hydrogen peroxide could not be detected until the electrolysis has been continued for three quarters of an hour, during which the pH of the solution was still below 6.0. Then the pH rose quickly and reached above 7.0 some five minutes later; thereafter hydrogen peroxide was found always present.

The reaction expressed by the second equation of the chemical change (2) is reversible as was pointed out by W.H. Hatcher and G.W. Holden.⁽¹⁾ If so, it is easily conceivable that the formation of hydrogen peroxide according to the second equation is governed by the condition of the electrolyte, in such a manner that an alkaline or a dilute solution favours the formation of hydrogen peroxide, while an acidic or a concentrated one acts contrarily.

The reason, why hydrogen peroxide became detectable after having been absent for the first 45 minutes of electrolysis, can be easily understood, if we take into consideration the pH value of the solution on the one hand

(1) *Trans. Roy. Soc. Canada* [3] **21**, Sect. III. (1927), 237—243 : C. 1928, I, 1929.

and the concentration of it on the other. The following table and Fig. 2 relate to the solution of KAc 10.0 gr. and HAc 2.8 gr. per 100 c.c.

Table 4.

Electrolyte, (KAc 10.0 gr. + HAc 2.8 gr.) per 100 c.c.,
Original pH=5.0, $D_A=10$ A/dm², Temp.=8–10°C.

Duration of electrolysis	After electrolysis			
	pH	H ₂ O ₂	KMnO ₄	KI+starch
$\frac{1}{2}$ hour	5.1	abs.	5 drops	Thiosulphate 2 drops
$1\frac{1}{2}$	6.9	"	10	7
$1\frac{2}{3}$	7.4	pres.	17	14
2	8.7	"	2 c.c.	8
3	"	"	10	26
4	"	"	40	8.6 c.c.
5	"	"	110	21.6
6	8.65	"	105	25.9
8	8.55	"	150	18.6

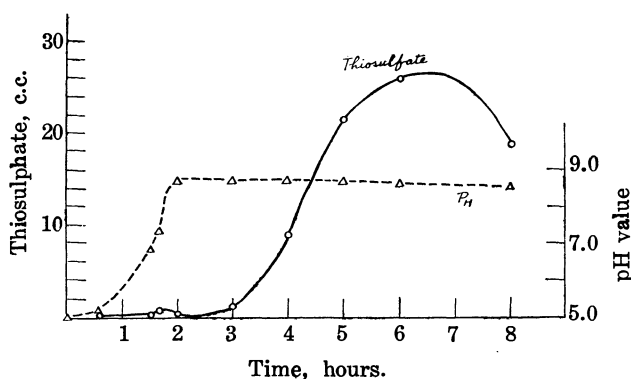


Fig. 2.

(KAc 10.0 gr. per 100 c.c.) solution, $D_A=10$ A/dm², Temp.=8–10°C.

By the same reason as with the previous case it can be assumed that the ethane evolution from the present solution reaches the maximum point somewhere between $1\frac{1}{2}$ –2 hours after the commencement of electrolysis; after that it gradually falls until it is nearly done with about an hour later.

Let us now proceed to examine the thiosulphate curve of Fig. 2. After passing a maximum point the curve falls to a minimum point two hours after the start; and then it suddenly leaps up to another maximum point again. The maximum value of thiosulphate consumption is 26.5 c.c. in this case, whereas it was 16.5 c.c. in the preceding one.

It will be readily seen that the maximum point of the ethane formation curve thus coincides with the minimum point of the thiosulphate consumption curve, and the lowest part of the former corresponds with the highest part of the latter. Besides, the maximum value of thiosulphate consumption of the second KAc solution is much higher than that of the first one, although not so high as proportional to the concentration (*loc. cit.*).

These facts will demonstrate, the author is confident, that ethane has its origin in acetyl peroxide.

Table 5 and Fig. 3 shown below illustrate the results of the electrolysis of the solution containing KAc 20 gr. and HAc 5.6 gr. in 100 c.c. The ethane curve in this figure does not represent this solution but that containing 20% KAc and 5% HAc instead (the first paper, *loc. cit.*). But the difference between these two solutions being very slight, the curve may be taken as that of the former without significant error.

Table 5.

Electrolyte, (KAc 20.0 gr. + HAc 5.6 gr.) per 100 c.c.,
Original pH = 5.1, $D_A = 10$ A/dm², Temp. = 8–10°C.

Duration of electrolysis	After electrolysis			
	pH	H ₂ O ₂	KMnO ₄	KI+starch
$\frac{1}{4}$ hour	5.15	abs.	5 drops	Thiosulphate 1 drop
2 $\frac{1}{2}$	5.7	"	—	3
3	7.5	"	12	9
4	8.7	pres.	2.0 c.c.	5
5	"	"	5.5	9
8	8.8	"	120	12.5 c.c.
10	8.7	"	145	14.7
13	8.5	"	220	31.5
16	—	"	270	18.9

Coincidences between several corresponding points on the ethane and thiosulphate curves can clearly be noticed here. The maximum value of thiosulphate consumption is 31.5 c.c., being greater than those of the fore-

going two solutions. The hours needed for the attainment of these maximum points were nearly proportional to the concentration of the electrolytes; being 4, 6.5 and 13 hours respectively in these three cases.

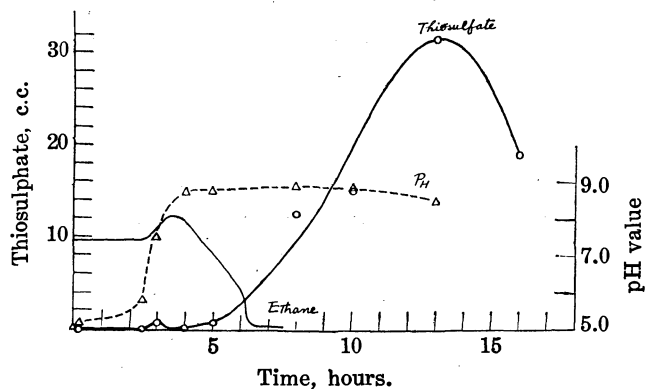


Fig. 3.

(KAc 20.0 gr. per 100 c.c.) solution, $D_A = 10 \text{ A/dm}^2$, Temp. = $8-10^\circ\text{C}$.

This fact upholds once more, it seems, that acetyl peroxide is one of the principal products of the electrolysis of potassium acetate solutions.

Table 6.

Electrolyte, (KAc 40.0 gr. + HAc 12.0 gr.) per 100 c.c.,
Original pH = 5.1, $D_A = 10 \text{ A/dm}^2$, Temp. = $8-10^\circ\text{C}$.

Duration of electrolysis	After electrolysis			
	pH	H ₂ O ₂	KMnO ₄	KI+starch
$\frac{1}{2}$ hour	5.15	abs.	16 drops	Thiosulphate 4 drops
$5\frac{1}{2}$	6.0	„	37	10
$6\frac{1}{2}$	7.3	„	35	17
8	9.0	„	32	9
$9\frac{3}{4}$	9.3	„	15	20

The electrolysis of the (KAc 40 gr. + HAc 12 gr.) per 100 c.c. solution has been traced only so far as 9 hours after the start. The minimum point of thiosulphate consumption lies, at least in this limited range of electrolysis, perhaps at a period of about 8 hours after the start, a fact which can be readily estimated from the foregoing data.

No hydrogen peroxide was detected in this case, even after nearly 10 hours' operation, when the pH value was already as high as 9.3. In the case of the (KAc 20 gr. + HAc 5.6 gr.) per 100 c.c. solution hydrogen peroxide was detected at pH = 8.2, but not at pH = 7.5 yet. In the case of the (KAc 10 gr. + HAc 2.8 gr.) per 100 c.c. solution hydrogen peroxide was detected at pH = 7.4, but not at pH = 6.9 yet. In the case of the (KAc 5.0 gr. + HAc 1.4 gr.) per 100 c.c. solution, it was detected at pH = 7.3, but not at pH = 5.9 yet.

Hydrogen peroxide, which is one of the most interesting compounds, not only from the scientific, but technical, view, is considered so far not to be produced by the anodic reaction directly.

If we assume that hydrogen peroxide makes its appearance according to the equations (2) we can easily understand, by admitting the explanation given above, the relation between its formation and pH value in each of these solutions, and also the fact that the more concentrated are the solutions, the less capable are they of forming H_2O_2 in spite of a comparatively higher value of pH.

The author made an observation in the first paper that a potassium acetate solution containing ammonium carbonate behaves quite differently from other cases under electrolysis, with extraordinarily small but constant yields of ethane and oxygen throughout the process; the second paper was concerned to somewhat detailed examinations of a similar nature. The following table deals with electrolysis of (KAc 10 gr. + Amm. carbonate 5 gr.) per 100 c.c. solution.

Table 7.

Electrolyte, (KAc 10.0 gr. + Amm. carbonate 5.0 gr.) per 100 c.c.,
Original pH = 8.6, $D_A = 10 \text{ A/dm}^2$, Temp. = 8–10°C.

Duration of electrolysis	After electrolysis			
	pH	H_2O_2	$KMnO_4$	KI+starch
0 hour	8.6	—	—	Thiosulphate 0 drop
1	„	pres.	35 c.c.	10
2½	„	„	70	1.3 c.c.
5	8.5	„	250	3.3
7	„	„	125	7.5
9	8.1	„	160	10.4

The comparatively higher value of the original pH of this solution makes us understand that hydrogen peroxide is formed shortly after the start of electrolysis.

Extraordinarily efficient internal oxidation of this solution (vid. the first paper), by corresponding with the very small yields of ethane and oxygen, signifies that a large amount of methyl alcohol is formed there. The more of the $\text{CH}_3\cdot\text{COO}$ group of the acetate is changed into the form of methyl alcohol, the less will take the form of ethane or acetyl peroxide, the latter of which may be further transformed into hydrogen peroxide. The comparatively smaller amounts of ethane (vid. the second paper) and thiosulphate consumption in Table 7 both conform to this expectation.

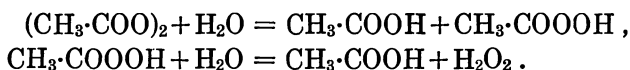
In conclusion of this paper the author begs to express his deepest sense of indebtedness to Professor Dr. M. Matsui of Kyoto Imperial University for his unfailing encouragement and suggestions for the continuation of these studies.

Summary.

(1) The relation between ethane and oxidizing substances in the solutions formed by the electrolyses of acetate solutions is discussed.

(2) It is demonstrated that acetyl peroxide is first formed at the anode, and that ethane is one of its decomposition products.

(3) The presence of hydrogen peroxide in the solutions after electrolysis is attributed to the following hydrolyses of acetyl peroxide:



(4) It is discussed how the formation of hydrogen peroxide is related to the pH value of the solution on the one hand and to the concentration of the solution on the other.

(5) The relation existing between the ethane and the hydrogen peroxide formations is also discussed.

(6) It is concluded that the facts observed in the experiments so far carried out by the writer can well be explained by assuming the intermediate formation of acetyl peroxide.

Tokushima Technical College,
Tokushima.

DAS VERHALTEN DER PYRIDINGRUPPE BEI DER ELEKTROCHEMISCHEN OXYDATION.

I. PYRIDIN.

Von Moriaki YOKOYAMA und Kazuo YAMAMOTO.

Eingegangen am 22. November, 1931. Ausgegeben am 28. Januar, 1932.

Dass das Pyridin und der Pyridinkern in seinem chemischen Verhalten durch grosse Beständigkeit ausgezeichnet ist, ist allgemein bekannt. Es kann mit konzentrierter Salpetersäure oder Chromsäure gekocht werden ohne Zersetzung zu erleiden⁽¹⁾; auch von salpetriger Säure wird es nicht verändert⁽²⁾. Neuberg⁽³⁾ erhielt wahrscheinlich Pentose neben viel unverändertem Pyridin mit Wasserstoffsuperoxyd in saurerer Lösung bei Gegenwart von Ferrosulfat. In neuerer Zeit konnten M. Delépine⁽⁴⁾ und B.D. Shaw u. A.L. Wilkie⁽⁵⁾ Pyridin mit Kaliumpermanganat in saurerer oder alkalischer Lösung zersetzen. J. Dorronsoro⁽⁶⁾ erhielt auch Ammoniak und Kohlendioxyd daraus bei Oxydation mit Natriumpersulfat in saurerer Lösung. All diese Forscher kamen aber nur bei erhöhter Temperatur zum Ziele.

Die elektrochemische Oxydation von Pyridin, bezw. des Pyridinkernes ist jedoch bis jetzt nicht untersucht worden. Ferner ist schon oft bei Gelegenheit der Schilderung elektrochemischer Oxydation organischer Verbindungen darauf hingewiesen worden, dass der anodischen Sauerstoff eines der wirksamsten, wenn nicht das wirksamste Oxydationsmittel überhaupt ist. Daher interessierte es uns zu studieren, wie das Verhalten von Pyridin, resp. des Pyridinkerns bei Einwirkung von anodischen Sauerstoff ist.

Beschreibung der Versuche.

4 cm³ (3,96 gr.) Pyridin (von Kahlbaum; sp. Gew. 0.981; Sdp. 116°C.) wurden in 150 cm³ 2n. Schwefelsäure gelöst, und in der Tonzelle an einer zylindrischen Bleianode⁽⁷⁾ (mit vorher frisch hergestelltem Bleidioxyd-Ueberzug) mit der anodischen Stomdichte von 0.05 Amp/cm² bei 68°C. unter starker Rührung elektro-oxydiert; die Kathode war ein Platinblech, der Katolyt 2n. Schwefelsäure, und die Strommenge 20F/Mol., welche etwas

(1) Anderson, *Ann.*, **105** (1858), 339.

(2) Oechsner de Coninck, *Bull. Soc. Chem.*, [2], **43** (1885), 180.

(3) *Biochem. Z.*, **184**, (1927), 206.

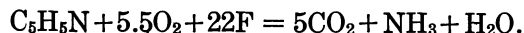
(4) *Compt. rend.*, **184**, (1927), 206.

(5) *J. Chem. Soc.*, **130** (1928), 1377.

(6) *Chem. Centr.* 1928, II, 1192; *Anales Soc. Espanola Fisica Quim.*, **25** (1927), 409.

(7) Bei elektrochemischer Oxydation an Pt-anoden beobachten wir die Entstehung der gleichen Produkten, jedoch in niedrigerer Stromausbeute.

niedriger ist als die theoretische Strommenge bei völligem Abbau nach der Gleichung



Im Verlauf der Elektrolyse wurde der Anolyt ein wenig bräunlichgelb gefärbt.

A. Die gasförmigen Reaktionsprodukte. Während des Verlaufes der Elektrolyse wurden die in dem Anodenraum entwickelten Gase möglichst sorgfältig analysiert. Denn die dauernde Kontrolle der qualitativen Beschaffenheit der Anodengase während des ganzen Verlaufs der Elektrolyse erschien geeignet, ein klares Bild von der Art und dem Verlauf des Oxydationsprozesses zu vermitteln. Die Gasanalysenmethode wurde nach E. Müller⁽¹⁾ einmal pro Stunde durchgeführt. Wir gebrauchten 3 Hempelsche Pipetten, welche mit den Absorptionsmitteln⁽²⁾ für Sauerstoff, Kohlendioxyd und Kohlenmonoxyd gefüllt waren.

Einige Analysenresultate aus der grossen Reihe der durchgeführten Versuche wurden in der folgenden Tabelle zusammengestellt. Die Gasvolumina wurde darin auf 0°C. und 760 mm. Druck reduziert. Als Sperrflüssigkeit der Messapparatur diente gesättigte, Kohlendioxyd praktisch nicht absorbierende Natriumchloridlösung⁽³⁾.

Tabelle 1.

Stromstärke: 2 Amp. Stromdichte: 0.05 Amp./cm².

Temperatur: 68°C.

Stunden	Sauerstoff- volumina des O ₂ - coulometers ccm.	Aufgefan- gene gasf. Produkte ccm.	Zusammensetzung des Anodengases (%)			Ver- brauchter Sauerstoff. ccm.	Strom- ausbeute
			CO ₂	CO	O ₂		
1	80.7	62.6	22.9	0	77.1	32.4	40.2
2	80.7	68.8	26.6	0	73.4	30.3	37.8
3	80.1	70.8	27.4	0.1	72.5	28.8	36.0
4	80.7	71.0	26.1	0.1	73.8	27.4	34.0
5	80.1	72.3	25.2	0.1	74.7	26.1	32.6
6	80.1	76.9	24.0	0.1	75.1	22.5	28.1
7	80.4	72.7	20.5	0.2	79.3	22.8	29.9
8	78.6	72.2	20.8	0.2	79.0	21.6	27.5
9	81.0	74.4	19.6	0.2	80.2	21.3	26.3
10	80.7	75.0	18.5	0.3	81.2	19.8	24.5
11	80.7	75.4	16.9	0.3	82.8	18.3	22.7
12	80.3	77.2	16.8	0.3	82.9	17.4	21.4
13	81.0	76.6	15.1	0.3	84.6	16.2	20.0

(1) Müller, Elektrochem. Praktikum, 4 Aufl., S., 155.

(2) Yokoyama u. Ishikawa, Dieses Bulletin, **6** (1931), 277.

(3) G. Hoffmann, Z. angew. Chem., **39** (1926), 401.

Tabelle 2.

Stromstärke: 2 Amp. Stromdichte: 0.05 Amp./cm².
Temperatur: 20°C.

Stunden	Sauerstoff- volumina des O ₂ - coulometers ccm.	Aufgefan- gene gasf. Produkte ccm.	Zusammensetzung des Anodengases (%)			Ver- brauchter Sauerstoff. ccm.	Strom- ausbeute
			CO ₂	CO	O ₂		
1	80.8	63.9	6.4	0	83.6	27.4	34.0
2	80.6	69.9	7.9	0	92.0	16.5	20.5
3	80.1	71.7	8.4	0.1	91.5	14.6	18.5
4	80.7	74.0	8.4	0.1	91.5	13.1	16.5
5	80.2	75.2	7.8	0.1	92.1	12.4	15.5
6	80.1	76.0	7.6	0.2	92.2	10.8	13.5
7	80.4	76.8	6.4	0.2	93.4	8.6	10.7
8	80.2	77.2	6.1	0.2	93.7	7.8	9.9
9	80.2	77.5	5.9	0.2	93.9	7.5	9.0
10	80.7	77.0	5.5	0.2	94.3	7.4	9.2
11	80.8	78.0	5.1	0.3	94.6	6.9	8.6
12	81.2	78.5	4.8	0.3	94.9	6.8	8.4
13	81.1	79.1	4.7	0.3	95.0	6.0	7.4

Tabelle 3.

Stromstärke: 4 Amp. Stromdichte: 0.1 Amp./cm².
Temperatur: 68°C.

Stunden	Sauerstoff- volumina des O ₂ - coulometers ccm.	Aufgegan- ene gasf. Produkte ccm.	Zusammensetzung des Anodengases (%)			Ver- brauchter Sauerstoff. ccm.	Strom- ausbeute
			CO ₂	CO	O ₂		
1	81.6	68.1	20.9	0.1	79.0	25.5	31.3
2	81.6	73.8	23.5	0.1	79.4	25.2	30.8
3	81.6	77.1	20.2	0.2	79.6	21.0	25.7
4	81.6	77.7	19.5	0.2	80.3	19.2	23.5
5	80.7	77.4	13.3	0.3	83.4	16.2	20.1
6	80.1	77.7	13.2	0.3	86.5	12.9	16.1
7	81.0	79.6	11.1	0.3	88.6	11.4	14.1

Tabelle 4.

Stromstärke: 0.4 Amp. Stromdichte: 0.01 Amp./cm².

Temperature: 68°C.

Stunden	Sauerstoff- volumina des O ₂ - coulometers ccm.	Aufgefan- gene gasf. Produkte ccm.	Zusammensetzung des Anodengases (%)			Ver- brauchter Sauerstoff. ccm.	Strom- ausbeute
			CO ₂	CO	O ₂		
1	84.0	40.1	21.7	0	78.3	51.6	61.4
2	80.1	62.1	25.0	0	75.0	38.1	47.5
3	78.9	67.9	31.2	0.1	68.7	33.3	42.1
4	78.9	64.7	30.5	0.1	69.3	32.1	39.3
5	79.5	70.7	26.7	0.2	73.1	27.9	35.0
6	79.2	69.8	25.8	0.2	74.0	26.4	33.3
7	79.8	71.3	24.4	0.2	75.2	26.7	32.7
8	79.5	70.7	23.3	0.2	76.5	25.5	32.1
9	79.5	69.5	22.0	0.2	77.8	25.5	32.1
10	80.1	72.3	21.2	0.2	78.6	25.5	31.9
14	81.0	70.8	20.5	0.2	79.3	24.0	30.0
20	79.8	67.4	15.6	0.2	84.2	22.1	28.9
40	81.9	72.5	14.1	0.2	85.7	19.8	24.2

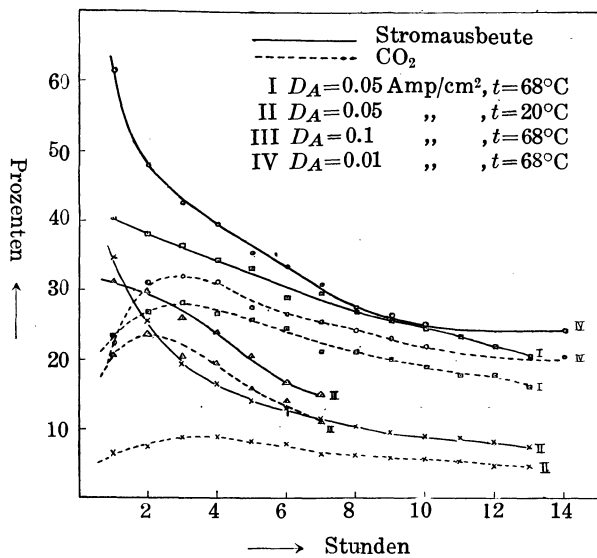


Fig. 1.

Wie aus der Tabelle (1)–(4) und den Kurven (Fig. 1) ersichtlich ist, sind Kohlendioxyd und wenig Kohlenmonoxyd im Anodengase enthalten, das Verhalten des Anodengases je nach der Elektrolysebedingungen unterschiedlich und die am Anfang erwähnten Bedingungen die besserer, sodass wir auch bei den meisten Versuchen diese Bedingungen einhalten.

B. Die in Aether leicht löslichen Produkte. Nach der Elektrolyse wurde der Anolyt zunächst mit Aether mehrmals ausgeschüttelt. Die Aetherlösung hinterliess nach dem Abdestillieren des Aethers eine stechend nach Ameisensäure riehende, etwas gelb gefärbte Flüssigkeit, die gegen Lackmus sauer reagierte, aus Mercurichlorid Mercurochlorid abschied und Permanganatlösung entfärbte. Sie wurde mit Bariumcarbonatbrei neutralisiert und filtriert um überschüssiges Bariumcarbonat zu entfernen. Nach Verdampfen des Filtrats erhielten wir Bariumformiat. (Ausbeute: etwa 0.05 gr. pro Versuch).

Das Bariumsalz, das im Verlauf von 10 Einzelversuchen aufgesammelt wurde, nach dem Reinigen mit Tierkohle und Umkrystallisieren im Vakuum über Schwefelsäure bis zur Gewichtkonstanz getrocknet und analysiert.

0.1553 gr. gaben nach Abrauchen mit Schwefelsäure 0.1589 gr. BaSO_4 . Gef. Ba = 60.20%
Ber. für $(\text{CHO}_2)_2 \text{Ba}$: Ba = 60.42%

C. Die mit Wasserdampf nicht flüchtigen Produkte. Die mit Aether extrahierte Lösung des Anolyten wurde zuerst mit Bariumhydroxydlösung und am Ende mit Bariumcarbonat vorsichtig neutralisiert und dadurch von Schwefelsäure vollständig befreit. Die so erhaltene filtrierte Lösung wurde im Wasserdampfstrom langsam, bis das Destillat gegen Nessler'sches Reagenz nicht mehr reagierte, destilliert, wobei der Aufnahmekolben etwa 100 ccm Wasser enthielt und mit Eis von aussen gekühlt wurde um flüchtige Gase leicht aufzufangen.

Der etwa gelbegefärbte Rückstand der Wasserdampfdestillation wurde im Vakuum zur Trockne eindampft. Er hinterliess ein hellgelb gefärbtes krystallinisches Produkt. Aus seiner wässrigen Lösung wurde nach Filtrieren und Reinigen mit Tierkohle schöne weisse prismatische Nadeln erhalten, die durch die typischen Reaktionen als Bariumnitrat identifiziert wurden. (Ausbeute: 0.5 gr.).

D. Die mit Wasserdampf flüchtigen Produkte. Das Destillat der Wasserdampfdestillation, das gegen Lackmus schwach alkalisch reagierte, wurde mit Salzsäure neutralisiert und dann im Vakuum bis zur vollständigen Trockne zur Befreiung von Pyridinhydrochlorid eingedampft. Wir erhielten dabei eine kleine Menge einer weissen krystallinischen Masse, die hygroskopisch war.

Sie wurde mit wenig Wasser aufgenommen, auf dem Wasserbad verdampft und hinterliess weisse nadelförmige krystalle, die mit absolutem Alkohol in einen unlöslichen Teil (a) und einen leicht löslichen Teil (b) zerlegt werden konnten.

(a) *Die in Alkohol unlösliche Substanz.* In der in Alkohol nicht löslichen Substanz konnte leicht Ammoniak nachgewiesen werden mit Hilfe der bekannten Geruchsprobe nach Zusatz von Kalilauge. Wir stellten nach dem Umkrystallisieren aus Wasser das Platinchloriddoppelsalz dar, dessen Analyse folgende Werte ergab.

0.1377 gr. Platindoppelsalz ergaben nach dem Glühen 0.0604 gr. Platin. Gef. Pt=43.86%
Ber. für $(\text{NH}_4)_2\text{PtCl}_6$: Pt=43.96%

Ausbeute: 0.15 gr.

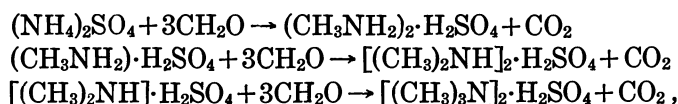
(b) *Die in Alkohol leicht löslichen Substanzen.* Die Alkohollösung hinterliess nach dem Verdampfen des Alkohols weisse Nadelkrystalle, die chlorhaltig und etwas hygroskopisch waren und bei 210°–237°C. schmolzen unter gleichzeitigem Sublimieren. Der fischartige Geruch nach dem Zusatz von Kalilauge liess auf Methylamin und seine Verwandten schliessen. Nach dem Umkrystallisieren aus Alkohol und Trocknen über Schwefelsäure im Vakuum wurde die krystalline Masse der Analyse unterworfen.

0.0971, 0.1455 gr. Subst. gaben mit AgNO_3 0.1809, 0.2715 gr. AgCl . Gef. Cl = 46.78, 46.16%.

Berechnet sich für Methylaminchlorid 52.52%Cl; für Dimethylaminchlorid 43.49%Cl; für Trimethylaminchlorid 37.11%Cl.

Diesen Beobachtungen nach handelt es sich vermutlich um eine Mischung der Hydrochloride von Methylamin und seine Verwandten.

Wie lässt sich aber die Bildung von Methylamin und seiner Verwandten erklären? Sie scheint zunächst schwer verständlich, aber mit Hilfe folgender Ueberlegung könnte man sich die Bildung vorstellen. Wir nehmen an, dass durch den Angriff der Pyridinmolekel gleichzeitig Formaldehyd und Ammoniak, resp. Ammoniumsulfat entstehen. Die Stromwärme an der Anode veranlasst nun die Kondensation der beiden Substanzen nach J. Plöchl⁽¹⁾ nach folgenden Gleichungen

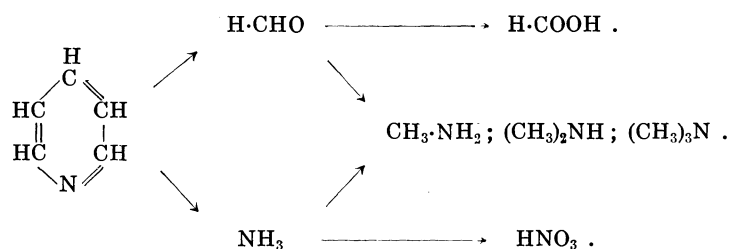


sodass in dem Anolyt ein Gemisch von Mono-, Di-, und Trimethylamin entsteht.

(1) *Ber.*, **21** (1888), 2117; vgl. H. Emde u. Hornemann, *Helv. Chim. Acta.*, **14** (1931), 892.

Wir hatten eine Mischung von Formaldehyd und Ammoniumsulfatlösung in einem Blindversuche elektro-oxydiert und in der Tat eine ähnliches Basengemisch darstellen können, wie wir es bei der elektrochemischen Oxydation von Pyridin erhalten hatten.

Unter Zusammenfassung aller Beobachtungen lässt sich einstweilen folgendes vorläufige Schema über den Oxydationsverlauf am Pyridinkern aufstellen wobei die letzten Stufen Kohlenmonoxyd und Kohlendioxyd noch nicht berücksichtigt sind); es lautet:



Zusammenfassung.

(1) Das gegen Hitze sowie gegen starke Oxydationsmittel sehr widerstandsfähige Pyridin wurde in seinem Verhalten gegen anodischen Sauerstoff untersucht.

(2) Bei der elektrochemischen Oxydation des Pyridins an der Bleidi-oxydanode in verdünnter Schwefelsäure erhält man die folgenden Oxydationsprodukte: Kohlendioxyd, Kohlenmonoxyd, Salpetersäure, Ameisensäure, Ammoniak und Formaldehyd, welch letzteres durch sofortige Kondensation mit Ammoniak Methylamin und seine Verwandten ergibt.

(3) Während der Analyse wurde der kinetische Verlauf der Gasabscheidung an der Anode unter verschiedenen Elektrolysebedingungen analytisch verfolgt.

Yokohama Technische Hochschule, Yokohama.

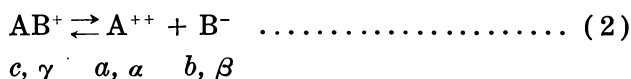
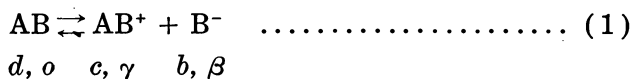
CONCENTRATION CELL WITH TERNARY ELECTROLYTE.

By Kosaku MASAKI

Received October 23rd, 1931. Published February 28th, 1932.

Since the electromotive force of the concentration cell with ternary electrolyte had been studied by H. M. Goodwin⁽¹⁾ in 1894, it was studied by many investigators.⁽²⁾ But there is no information on the theoretical determination of the electromotive force of the cell except the work by J. E. Geissler.⁽³⁾

He assumed the following two reversible reactions in the next cell.



where a, b, c, d are the ionic concentrations and α, β, γ are the transport number of each ions and also he showed that when the mentioned two reversible reactions take place in the cell A, the electromotive force of the cell is

$$e = -\frac{RT}{F} \left[\left(m + \frac{\beta - \gamma}{\beta + \gamma} \right) \ln \frac{a_2}{a_1} + \left(m - \frac{\alpha - \gamma}{2\alpha - \gamma} \right) \ln \frac{b_2}{b_1} + \left(-m + \frac{\alpha - \beta}{2\alpha + \beta} \right) \ln \frac{c_2}{c_1} \right. \\ \left. + \left(-\frac{\beta - \gamma}{\beta + \gamma} + \frac{\alpha - \gamma}{2\alpha - \gamma} - \frac{\alpha - \beta}{2\alpha + \beta} \right) \ln \frac{x_1}{x_2} \right] \quad \dots\dots\dots (3)$$

where x_1, x_2 are the specific conductance of c_1 and c_2 and the value of m is

$$m = \frac{(2\alpha + \beta)(-8\alpha - \beta + 3\gamma)}{(2\alpha + \gamma)(\beta + \gamma)} \quad \dots\dots\dots (4)$$

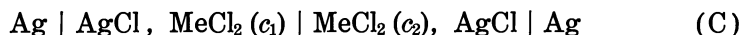
(1) *Z. physik. Chem.*, **13** (1894), 577.

(2) W. Consad, Dissert. V. Gottingen 1903; E. Biron, *J. Russ. physik. Chem.*, **39** (1908), 1506; **40** (1908), 79; E. Biron and Afranasjer, *J. Russ. physik. Chem.*, **41** (1909), 1175; J. N. Pearce and R. W. Gelbach, *J. physik. Chem.*, **29** (1925), 1023.

(3) *Z. Elektrochem.*, **18** (1912), 135.

Measurements of the electromotive force had been studied to confirm of the existence of AB^+ ion in the mentioned electrolyte, and also he calculated the electromotive force of the cell A by assuming the value of γ , for example, $\gamma = 20$ or $\gamma = 10$.

In this investigation the electromotive force of the following cells were studied in the very dilute solution and also the theoretical value of the electromotive force was calculated.



where Me are magnesium, calcium, strontium, barium and zinc.

Experimental.

Chlorides of magnesium, calcium, strontium, barium and zinc used were of Kahlbaum and purified by recrystallization, and also calomel were of Kahlbaum and purified by washing with conductivity water.

Silver chloride was prepared from the dilute solution of corresponding potassium chloride (Kahlbaum) by precipitating with purified silver nitrate at the dark room. Silver electrode was prepared by electrolyzing a one percent solution of pure potassium silver cyanide with pure silver wire as a cathode. Mercury used was of purified by vacuum distillation from the commercial mercury. The amalgams were made by electrolyzing a 10 % solution of pure chlorides of zinc, barium, strontium and calcium with mercury as a cathode in the hydrogen atmosphere.

The cells were of ordinary form. All the electromotive force measurements were carried out after the cells was kept for about one hour in a thermostat at a constant temperature, the variation of which was regulated within 0.05°C . For the measurements a potentiometer and a D.L. type mirror galvanometer were used. Constants necessary for the calculation are given in the following tables.

The values of mobility at 18°C . were taken from the results of Noyes and Falk⁽¹⁾ and also were calculated from the values of A_∞ for the salts. The values at 30°C . were calculated from the following equations.

$$C = \frac{(lt_2 - lt_1)}{(t_2 - t_1)l} \dots\dots\dots (5)$$

(1) *J. Am. Chem. Soc.*, **34**(1912), 454.

$$l = (lt_2 + lt_1)2 \dots\dots\dots (6)$$

where lt_2 , lt_1 , are mobilities at t_2 , t_1 .

Table 1.
Mobilities of the Various Ions.

Ion	Mobility		Temperature coefficient $C \times 10^4$
	18°C	30°C	
$\frac{1}{2}\text{Zn}^{++}$	47.0	63.9	254
$\frac{1}{2}\text{Sr}^{++}$	51.9	70.2	247
$\frac{1}{2}\text{Ca}^{++}$	51.9	70.2	247
$\frac{1}{2}\text{Ba}^{++}$	55.4	80.2	239
$\frac{1}{2}\text{Mg}^{++}$	45.9	55.6	256
Cl^-	65.5	85.0	216

Table 2.
Activity Coefficients of Chlorine Ion at Various Concentrations.

Molarity	0.1	0.05	0.02	0.01	0.005	0.004	0.003	0.0025	0.002	0.00125	0.001	0.0005	0.00025
Activity coefficient	0.79	0.84	0.89	0.92	0.95	0.955	0.965	0.967	0.97	0.975	0.98	0.985	0.99

Table 3.
Activity Coefficients of Ions of Zinc, Strontium, Calcium and
Barium at Various Concentrations.

Molarity	0.05	0.025	0.02	0.01	0.005	0.0025	0.00125	0.000625
Activity coefficient	0.34	0.43	0.46	0.53	0.60	0.66	0.73	0.775

These values in Tables 2 and 3 were calculated from the Table 8 of "Thermodynamics" by Lewis and Randall, and the values of ion concentration were calculated from the general formula :

$$\mu = \frac{Z_a^2(a) + Z_b^2(b) + Z_c^2(c)}{2} \dots\dots\dots (7)$$

where Z_a , Z_b , Z_c , are the valencies of ions and a , b , c are the ion concentrations.

Calculation of the Electromotive Force. At the mentioned concentration cell with ternary electrolyte, in the very dilute solution, if the concentration $c = 0$, from the equation (4) we will obtain as follows.

$$a = \frac{b}{2} \quad \text{and} \quad m = \frac{\alpha - \beta}{2\alpha + \beta}$$

Therefore,

$$\frac{a_2}{a_1} = \frac{b_2}{b_1} = \frac{x_2}{x_1}$$

So, the next equation derived from the equation (3)

$$e = -\frac{RT}{F} \frac{\alpha - \beta}{2\alpha + \beta} \ln \frac{b_2}{b_1} = -\frac{RT}{F} \frac{\alpha - \beta}{2\alpha + \beta} \ln \frac{a_2}{a_1} \dots\dots\dots (8)$$

If it is the concentration cell with regard to anion reversible, we have

$$e = -\frac{RT}{F} \frac{3\alpha}{2\alpha + \beta} \ln \frac{b_2}{b_1} \dots\dots\dots (9)$$

and also, if it is the concentration cell with regard to cation reversible, we have

$$e = \frac{RT}{F} \frac{3\beta}{2(2\alpha + \beta)} \ln \frac{a_2}{a_1} \dots\dots\dots (10)$$

If l_k , l_a are the mobilities of the two ions, the next equation may be obtained from the Kohlraush's theory.

$$\frac{l_k}{l_a} = \frac{\beta}{\alpha} \quad \text{or} \quad \frac{l_k}{\beta} = \frac{l_a}{\alpha} \dots\dots\dots (11)$$

Hence, if we put the equation (11) equal to $\frac{1}{K}$ (K : constant)

$$\frac{l_k}{\beta} = \frac{l_a}{\alpha} = \frac{1}{K}$$

so, $\alpha = Kl_a$ or $\beta = Kl_k \dots\dots\dots (12)$

by substituting these values to the equation (9), we get

$$e = -\frac{RT}{F} \frac{3Kl_a}{2Kl_a + Kl_k} \ln \frac{b_2}{b_1}$$

by simplification,

$$e = -\frac{RT}{F} \frac{3l_a}{2l_a + l_k} \ln \frac{b_2}{b_1} \dots\dots\dots (13)$$

Therefore, we obtained the following formula from the equation (13)

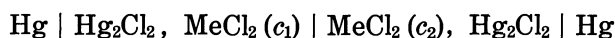
$$e = -\frac{RT}{F} \frac{3l_a}{2l_a + l_k} \ln \frac{f_2 b_2}{f_1 b_1} \dots\dots\dots (14)$$

where f_1 , f_2 are activity coefficients of chlorine ion at the various concentrations, and also we obtained the next equation by substituting the values of (12) to the equation (10)

$$e = \frac{RT}{F} \frac{3l_k}{2(2l_a + l_k)} \ln \frac{f_4 a_2}{f_3 a_1} \dots\dots\dots (15)$$

where f_3 , f_4 are activity coefficients of Me^{++} ion at the various concentrations.

Electromotive Force of Anion Reversible cell with Mercury Electrode.
The combination of the cell was as follows.



A series of measurements were carried out on the cells of the solutions of the different concentrations. Each experiment was done after keeping the cell at 30°C. for about an hour. All equations in the following tables obtained from the equation (14).

Table 4.

E. M. F. of Cell : $\text{Hg} \mid \text{Hg}_2\text{Cl}_2, \text{ZnCl}_2 (c_1) \mid \text{ZnCl}_2 (c_2), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$

$$e = -0.065524 \log \frac{f_2 b_2}{f_1 b_1} .$$

Concentration of $\text{ZnCl}_2 (c_2)$	Concentration of $\text{ZnCl}_2 (c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	-0.01790	-0.01873
0.005	0.0025	-0.01835	-0.01879
0.0025	0.00125	-0.01882	-0.01919
0.00125	0.001	-0.00579	-0.00625

Table 5.

E. M. F. of Cell : $\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{SrCl}_2(c_1) | \text{SrCl}_2(c_2), \text{Hg}_2\text{Cl}_2 | \text{Hg}$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $\text{SrCl}_2(c_2)$	Concentration of $\text{SrCl}_2(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	—	—0.01821
0.005	0.0025	—	—0.01828
0.0025	0.00125	—0.01850	—0.01863
0.0025	0.002	—0.00589	—0.00601
0.002	0.001	—0.01853	—0.01861

Table 6.

E. M. F. of Cell : $\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{BaCl}_2(c_1) | \text{BaCl}_2(c_2), \text{Hg}_2\text{Cl}_2 | \text{Hg}$

$$e = -0.061244 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $\text{BaCl}_2(c_2)$	Concentration of $\text{BaCl}_2(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	—0.01619	—0.01751
0.005	0.0025	—0.01723	—0.01757
0.0025	0.00125	—0.01753	—0.01794
0.0025	0.001	—0.02380	—0.02382
0.002	0.001	—0.01785	—0.01788

Table 7.

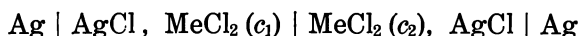
E. M. F. of Cell : $\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{CaCl}_2(c_1) | \text{CaCl}_2(c_2), \text{Hg}_2\text{Cl}_2 | \text{Hg}$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $\text{CaCl}_2(c_2)$	Concentration of $\text{CaCl}_2(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	—	—0.01821
0.005	0.0025	—0.01799	—0.01828
0.0025	0.002	—0.00593	—0.00601
0.0025	0.00125	—0.01875	—0.01863
0.002	0.001	—0.01853	—0.01861

From the data given in Tables 4, 5, 6 and 7, it will be found that the differences between the measured electromotive forces and calculated ones are 0.00043, 0.00011, 0.00017 and 0.00014 volt on 0.005 molal or more dilute solutions.

Electromotive Force of Anion Reversible cell with Silver Electrode.
The combination of the cell was as follows.



Silver chloride used was purified by washing several times with the electrolyte at a dark room to avoid the disturbing effect by sun beams. The measurements of the electromotive force of the cell were carried out at 30°C. and also in the dark. The results are summarized in the following tables.

Table 8.

E. M. F. of Cell: $\text{Ag} \mid \text{AgCl}, \text{ZnCl}_2 (c_1) \mid \text{ZnCl}_2 (c_2), \text{AgCl} \mid \text{Ag}$

$$e = -0.065524 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $\text{ZnCl}_2 (c_2)$	Concentration of $\text{ZnCl}_2 (c_1)$	E. M. F. in volt	
		Measured	Calculated
0.005	0.0025	—0.01866	—0.01879
0.0025	0.00125	—0.01895	—0.01919
0.01	0.005	—0.01877	—0.01883

Table 9.

E. M. F. of Cell: $\text{Ag} \mid \text{AgCl}, \text{CaCl}_2 (c_1) \mid \text{CaCl}_2 (c_2), \text{AgCl} \mid \text{Ag}$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $\text{CaCl}_2 (c_2)$	Concentration of $\text{CaCl}_2 (c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	—0.01834	—0.01821
0.005	0.0025	—0.01812	—0.01828
0.0025	0.00125	—0.01855	—0.01863

Table 10.

E. M. F. of Cell: $\text{Ag} | \text{AgCl}, \text{SrCl}_2(c_1) | \text{SrCl}_2(c_2), \text{AgCl} | \text{Ag}$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $\text{SrCl}_2(c_2)$	Concentration of $\text{SrCl}_2(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	−0.01811	−0.01821
0.005	0.0025	−0.01825	−0.01828
0.0025	0.00125	−0.01857	−0.01863

Table 11.

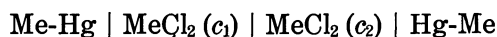
E. M. F. of Cell: $\text{Ag} | \text{AgCl}, \text{MgCl}_2(c_1) | \text{MgCl}_2(c_2), \text{AgCl} | \text{Ag}$

$$e = -0.06791 \log \frac{f_2 b_2}{f_1 b_1}$$

Concentration of $\text{MgCl}_2(c_2)$	Concentration of $\text{MgCl}_2(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.005	0.0025	−0.01899	−0.01948
0.0025	0.00125	−0.01983	−0.01989
0.00125	0.0006	—	−0.02016

From Tables 8, 9, 10 and 11, the differences between the measured E. M. F. and calculated ones are found 0.00018, 0.00012, 0.00004 and 0.00027 volt at lower molal solutions than 0.005 respectively. A larger value of difference than above will be found by using the more concentrated solution. In this investigation, it is very important to contact silver chloride with silver electrode.

E. M. F. of Cation Reversible cell with Amalgam Electrode. The cell used were of following type.



Preparation of amalgam was already mentioned. Prepared amalgam was carried into the acetone solution and shaken, then the amalgam was introduced into the cell which contained the electrolyte. Every measurement of the electromotive force of the cell was carried out after keeping it at 30°C. for about one hour. All equations in the following tables were obtained from the equation (15). The results are as follows.

Table 12.

E. M. F. of Cell : $\text{Zn-Hg} \mid \text{ZnCl}_2(c_1) \mid \text{ZnCl}_2(c_2) \mid \text{Hg-Zn}$

$$e = 0.02458 \log \frac{f_4 a_2}{f_3 a_1} .$$

Concentration of $\text{ZnCl}_2(c_2)$	Concentration of $\text{ZnCl}_2(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	0.00600	0.00588
0.005	0.0025	0.00615	0.00607
0.0025	0.00125	0.00655	0.00638
0.00125	0.000625	0.00638	0.00632

Table 13.

E. M. F. of Cell : $\text{Ba-Hg} \mid \text{BaCl}_2(c_1) \mid \text{BaCl}_2(c_2) \mid \text{Hg-Ba}$

$$e = 0.028897 \log \frac{f_4 a_2}{f_3 a_1} .$$

Concentration of $\text{BaCl}_2(c_2)$	Concentration of $\text{BaCl}_2(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	0.00700	0.00691
0.005	0.0025	0.00725	0.00713
0.0025	0.00125	0.00731	0.00750
0.00125	0.000625	0.00728	0.00743

Table 14.

E. M. F. of Cell : Ca-Hg | CaCl₂ (c₁) | CaCl₂ (c₂) | Hg-Ca

$$e = 0.026343 \log \frac{f_4 a_2}{f_3 a_1} .$$

Concentration of CaCl ₂ (c ₂)	Concentration of CaCl ₂ (c ₁)	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	0.00615	0.00630
0.005	0.0025	0.00639	0.00651
0.0025	0.00125	0.00675	0.00683
0.00125	0.000625	0.00664	0.00677

In these experiments, from Tables 12, 13 and 14, the differences between measured electromotive forces and calculated ones are found 0.00010, 0.00015 and 0.00011 volt at lower molal solutions than 0.005 molal respectively. It was found that amalgams have the disturbing effect in the presence of air. Therefore in these experiments, amalgam was introduced into the solution with keeping off from air.

Summary.

(1) The electromotive forces of the concentration cells with ternary electrolytes were studied by the three methods.

- (a) At anion reversible cell with mercury electrode.
- (b) At anion reversible cell with silver electrode.
- (c) At the cation reversible cell with amalgam electrode.

(2) Several equations were theoretically obtained to calculate the electromotive forces of the cells above mentioned.

(3) Mobilities at 30°C. and activity coefficients of chlorine, zinc, calcium, barium, strontium and magnesium ions were calculated.

(4) We had a very good agreement between measured electromotive forces and calculated ones in the very dilute solutions.

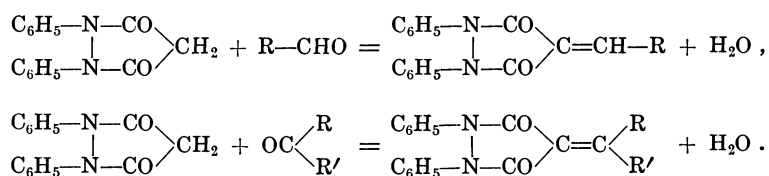
Yokohama Higher Technical School.

3, 5-DIKETOPYRAZOLIDINE DERIVATIVES. II.

By Tokuichi TSUMAKI.

Received December 5th, 1931. Published February 28th, 1932.

In the preceding paper,⁽¹⁾ it was reported as a property of 1, 2-diphenyl-3, 5-diketopyrazolidine that the compound condensed with aldehydes and ketones forming various coloured substances according to the following general formulae :—



And six condensation products were synthesised in the previous experiment. In this paper, another thirteen condensation products with aldehydes are reported. Their colours and melting points are described in the following table.

Aldehyde	Condensation product	M.P., °C	Colour
<i>p</i> -Tolylaldehyde	$\begin{array}{l} \text{C}_6\text{H}_5\text{—N—CO} \\ \text{C}_6\text{H}_5\text{—N—CO} \end{array} \text{C=CH—} \langle \text{C}_6\text{H}_4 \rangle \text{—CH}_3 \quad [1]$ 1, 2-Diphenyl-4-(<i>p</i> -methylbenzylidene)-3, 5-diketopyrazolidine	175	Yellow
Anisaldehyde	$\begin{array}{l} \text{C}_6\text{H}_5\text{—N—CO} \\ \text{C}_6\text{H}_5\text{—N—CO} \end{array} \text{C=CH—} \langle \text{C}_6\text{H}_4 \rangle \text{—OCH}_3 \quad [2]$ 1, 2-Diphenyl-4-(<i>p</i> -methoxybenzylidene)-3, 5-diketopyrazolidine	199	Yellow
<i>p</i> -Dimethylaminobenzaldehyde	$\begin{array}{l} \text{C}_6\text{H}_5\text{—N—CO} \\ \text{C}_6\text{H}_5\text{—N—CO} \end{array} \text{C=CH—} \langle \text{C}_6\text{H}_4 \rangle \text{—N} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \quad [3]$ 1, 2-Diphenyl-4-(<i>p</i> -dimethylaminobenzylidene)-3, 5-diketopyrazolidine	256 (decomposed)	Vermilion

(1) This Bulletin, 6 (1931), 1.

Aldehyde	Condensation product	M.P., °C	Colour
<i>p</i> -Hydroxybenzaldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{OH} \quad [4]$ 1,2-Diphenyl-4-(<i>p</i>-hydroxybenzylidene)-3,5-diketopyrazolidine	231-232	Yellowish brown
<i>m</i> -Hydroxybenzaldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{C}_6\text{H}_3(\text{OH}) \quad [5]$ 1,2-Diphenyl-4-(<i>m</i>-hydroxybenzylidene)-3,5-diketopyrazolidine	194	Reddish yellow
Salicylaldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{C}_6\text{H}_3(\text{OH})_2 \quad [6]$ 1,2-Diphenyl-4-(<i>o</i>-hydroxybenzylidene)-3,5-diketopyrazolidine	193	Reddish yellow
<i>p</i> -Nitrobenzaldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{NO}_2 \quad [7]$ 1,2-Diphenyl-4-(<i>p</i>-nitrobenzylidene)-3,5-diketopyrazolidine	243	Reddish brown
<i>m</i> -Nitrobenzaldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{C}_6\text{H}_3(\text{NO}_2) \quad [8]$ 1,2-Diphenyl-4-(<i>m</i>-nitrobenzylidene)-3,5-diketopyrazolidine	185	Russet
<i>o</i> -Nitrobenzaldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{C}_6\text{H}_3(\text{NO}_2) \quad [9]$ 1,2-Diphenyl-4-(<i>o</i>-nitrobenzylidene)-3,5-diketopyrazolidine	174-176	Reddish yellow
Protocatechu-aldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{C}_6\text{H}_2(\text{OH})_2 \quad [10]$ 1,2-Diphenyl-4-(3',4'-dihydroxybenzylidene)-3,5-diketopyrazolidine	255 (decomposed)	Yellow

Aldehyde	Condensation product	M.P., °C	Colour
Vanillin	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\langle \begin{array}{c} \text{---} \text{OH} \\ \text{---} \text{OCH}_3 \end{array} \right.$ [11] 1, 2-Diphenyl-4-(3'-methoxy-4'-hydroxy-benzylidene)-3, 5-diketopyrazolidine	156-157	Yellow
Piperonal	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\langle \begin{array}{c} \text{---} \text{O} \\ \text{---} \text{O}-\text{CH}_2 \end{array} \right.$ [12] 1, 2-Diphenyl-4-piperonylidene-3, 5-diketopyrazolidine	234-235	Yellow
Propionaldehyde	$\begin{array}{c} \text{C}_6\text{H}_5-\text{N}-\text{CO} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CO} \end{array} \rangle \text{C}=\text{CH}-\text{CH}_2-\text{CH}_3$ [13] 1, 2-Diphenyl-4-propylidene-3, 5-diketopyrazolidine	260 (decomposed)	Yellow

The properties and the methods of formation of these compounds are as follows.

1, 2-Diphenyl-4-(p-methylbenzylidene)-3, 5-diketopyrazolidine, [1]. When 0.8 gr. of 1, 2-diphenyl-3, 5-diketopyrazolidine and 1 gr. of *p*-tolylaldehyde were heated on the water-bath, a yellow mass was obtained. On recrystallization from alcohol, it gave yellow prismatic needles, which melts at 175°C. The yield was 1 gr.

Anal. Subst. = 0.0111 gr. ; $\text{N}_2 = 0.784$ c.c. (25°C., 754 mm.) (Pregl's method).

Found : N = 7.93%. Calc. for $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2$: N = 7.91%.

1, 2-Diphenyl-4-(p-methoxybenzylidene)-3, 5-diketopyrazolidine, [2]. When 0.6 gr. of diphenyldiketopyrazolidine and 0.8 gr. of anis-aldehyde were heated on the water-bath under stirring, reddish yellow mass was obtained. On recrystallization from alcohol, it gave yellow long needles. It is sparingly soluble in cold alcohol. The yield was 0.5 gr. M.p. : 199°C.

Anal. Subst. = 0.0173 gr. ; $\text{N}_2 = 1.202$ c.c. (26°C., 757 mm.) (Pregl's method).

Found : N = 7.80%. Calc. for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3$: N = 7.57%.

1, 2-Diphenyl-4-(p-dimethylamino-benzylidene)-3, 5-diketopyrazolidine, [3]. When 0.8 gr. of diphenyldiketopyrazolidine and 1 gr. of *p*-dimethylaminobenzaldehyde were mixed and heated on a water-bath for a few minutes, the mixture solidified to a mass of vermilion colour. It was well

washed with hot alcohol, and the condensation product was left in an almost pure state. It is soluble in benzene, sparingly soluble in hot alcohol. It melts at 256° C. Before melting it seems to be somewhat decomposed. The yield was 1 gr.

Anal. Subst. = 0.0125 gr.; N_2 = 1.205 c.c. (26°C., 759 mm.) (Pregl's method).
Found: N = 10.86%. Calc. for $C_{24}H_{21}O_2N_3$: N = 10.97%.

1, 2-Diphenyl-4-(p-hydroxybenzylidene)-3, 5-diketopyrazolidine, [4]. When 1 gr. of *p*-hydroxybenzaldehyde and 0.8 gr. of diphenyldiketopyrazolidine were fused together on a wire gauze, the mixture solidified to a reddish brown mass. On recrystallization from alcohol it gave yellowish brown prisms, which melts at 231°–232° C. The yield was 0.8 gr. The compound is soluble in benzene, sparingly soluble in cold alcohol, but insoluble in water. It is soluble in alkali solution giving it red colour.

Anal. Subst. = 0.0116 gr.; N_2 = 0.790 c.c. (25°C., 757 mm.) (Pregl's method).
Found: N = 7.67%. Calc. for $C_{22}H_{16}O_3N_2$: N = 7.87%.

1, 2-Diphenyl-4-(m-hydroxybenzylidene)-3, 5-diketopyrazolidine, [5]. When 0.5 gr. of *m*-hydroxybenzaldehyde and 0.5 gr. of diphenyl-diketopyrazolidine were heated on a wire gauze, a reddish brown viscous liquid was obtained, which on cooling solidified to a mass. On recrystallization from a small quantity of alcohol, it gave reddish yellow plates, which melts at 194° C. It is moderately soluble in alcohol. The yield was 0.4 gr.

Anal. Subst. = 0.0105 gr.; N_2 = 0.752 c.c. (28°C., 754 mm.) (Pregl's method).
Found: N = 7.96%. Calc. for $C_{22}H_{16}O_3N_2$: N = 7.87%.

1, 2-Diphenyl-4-(o-hydroxybenzylidene)-3, 5-diketopyrazolidine, [8]. When 0.8 gr. of 1, 2-diphenyl-3, 5-diketopyrazolidine and 1.7 gr. of salicylaldehyde were heated on the water-bath for about five minutes, the former dissolved into the latter forming brownish yellow solution, which solidified on cooling to a mass. It was pressed on a porous plate to remove the excess of salicylaldehyde, and was recrystallized from ethyl alcohol. The yield was 0.5 gr. The compound forms reddish yellow prisms, which melts at 193° C., and is moderately soluble in ethyl alcohol.

Anal. Subst. = 0.0107 gr.; N_2 = 0.757 c.c. (26°C., 761 mm.) (Pregl's method).
Found: N = 7.99%. Calc. for $C_{22}H_{16}O_3N_2$: N = 7.87%.

1, 2-Diphenyl-4-(p-nitrobenzylidene)-3, 5-diketopyrazolidine, [7]. When 1 gr. of *p*-nitrobenzaldehyde and 1 gr. of diphenyldiketopyrazolidine were heated at 110°C., a brownish black mass was obtained. It was purified by dissolving it in hot benzene and allowing it to stand after the addition of

ethyl alcohol. The compound crystallized out as reddish brown prisms. The yield was 0.8 gr. It melts at 243°C.; and is soluble in benzene and chloroform, and sparingly soluble in alcohol and ether.

Anal. Subst. = 0.0108 gr.; N_2 = 1.039 c.c. (25°C., 760 mm.) * (Pregl's method).
Found: N = 10.88%. Calc. for $C_{22}H_{15}O_4N_3$: N = 10.91%.

1, 2-Diphenyl-4-(*m*-nitrobenzylidene)-3, 5-diketopyrazolidine, [8]. One gram of *m*-nitrobenzaldehyde and 1 gr. of diphenyldiketopyrazolidine were heated on the water-bath for a few minutes. On cooling the product solidified to a mass of red colour. It was dissolved in hot alcohol and this solution gave russet crystals when allowed to stand for one day. They were recrystallized once from alcohol. M.p.: 185°C. The yield was 0.6 gr.

Anal. Subst. = 0.0113 gr.; N_2 = 1.137 c.c. (28°C., 755 mm.) (Pregl's method).
Found: N = 11.19%. Calc. for $C_{22}H_{15}O_4N_3$: N = 10.91%.

1, 2-Diphenyl-4-(*o*-nitrobenzylidene)-3, 5-diketopyrazolidine, [9]. One gram of *o*-nitrobenzaldehyde and 1 gr. of diphenyldiketopyrazolidine were fused. The product solidified on cooling to a mass, which gave the prismatic needles of reddish yellow colour on recrystallization from alcohol. The yield was 0.7 gr. M.p.: 174°–176°C.

Anal. Subst. = 0.0111 gr.; N_2 = 1.106 c.c. (28°C., 755 mm.) (Pregl's method).
Found: N = 11.09%. Calc. for $C_{22}H_{15}O_4N_3$: N = 10.91%.

1, 2-Diphenyl-4-(3', 4'-dihydroxybenzylidene)-3, 5-diketopyrazolidine, [10]. 1.2 Gr. of protocatechualdehyde and 1.2 gr. of 1, 2-diphenyl-3, 5-diketopyrazolidine were heated on a wire gauze above 150°C., and were kneaded into a mass. It was heated for a while with alcohol. The solution was coloured dark brown and the condensation product remained as a yellow precipitate. It was recrystallized from alcohol. The yield was 1.5 gr. M.p.: 255°C. Before melting it seems to be somewhat decomposed.

Anal. Subst. = 0.0116 gr.; N_2 = 0.811 c.c. (25°C., 749 mm.) (Pregl's method).
Found: N = 7.79%. Calc. for $C_{22}H_{16}O_4N_2$: N = 7.53%.

1, 2-Diphenyl-4-(3'-methoxy-4'-hydroxy-benzylidene)-3, 5-diketopyrazolidine, [11]. 1.2 Gr. of vanillin and 1.2 gr. of diphenyldiketopyrazolidine were fused on the water-bath and the product was dissolved in hot alcohol. This solution gave orange red crystals when allowed to stand for one day. On recrystallization from ligroin, the compound crystallized out as yellow crystals. It melts at 156°–157°C.; and the result of the analysis corresponds to the compound [11]. The yield was 1 gr.

Anal. Subst. = 0.0124 gr.; N_2 = 0.863 c.c. (27°C., 750 mm.) (Pregl's method).
Found: N = 7.72%. Calc. for $C_{23}H_{18}O_4N_2$: N = 7.25%.

1, 2-Diphenyl-4-piperonylidene-3, 5-diketopyrazolidine, [12]. When 1.2 gr. of piperonal and 1.2 gr. of diphenyldiketopyrazolidine were warmed on the water-bath under stirring, the whole changed into yellow powder. It was purified by dissolving it in hot chloroform and allowing it to stand after the addition of ethyl alcohol. The compound crystallized out as yellow needles. The yield was 1.6 gr. M.p.: 234°–235°C. It is soluble in ether, sparingly soluble in ethyl alcohol.

Anal. Subst. = 0.0152 gr.; N_2 = 1.029 c.c. (26°C., 760 mm.) (Pregl's method).
Found: N = 7.63%. Calc. for $C_{23}H_{16}O_4N_2$: N = 7.29%.

1, 2-Diphenyl-4-propylidene-3, 5-diketopyrazolidine, [13]. When 1 gr. of diphenyldiketopyrazolidine and 2 gr. of propionaldehyde were warmed on the water-bath for a while, the former dissolved into the latter forming brown solution. The excess of propionaldehyde was then evaporated off, and alcohol was added to the residue, and the solution was allowed to stand for one day. The condensation product deposited out as yellow crystals. It was filtered and washed with alcohol. The yield was 0.15 gr. It melts at 260°C. Before melting, it seems to be somewhat decomposed.

Anal. Subst. = 0.0107 gr.; N = 0.921 c.c. (28°C., 755 mm.) (Pregl's method).
Found: N = 9.58%. Calc. for $C_{18}H_{16}O_2N_2$: N = 9.59%.

The Osaka High School, Osaka.

ON THE REACTION BETWEEN ALIZARIN AND SODIUM ALUMINATE IN AQUEOUS SOLUTION.

By Seigo MATSUOKA.

Received December 19th, 1931. Published February 28th, 1932.

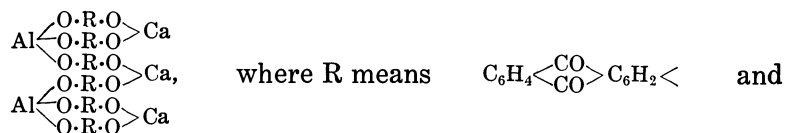
Hitherto many chemists studied the composition of the turkey-red, the formula $2\text{Al}_2\text{O}_3 : 3\text{CaO} : \text{C}_{14}\text{H}_8\text{O}_4$ was proposed by Rosenstiehl⁽¹⁾; the formula $\text{Al}_2\text{O}_3(\text{CaO})_2(\text{C}_{14}\text{H}_6\text{O}_3)_5$ by Saget⁽²⁾; Al_2O_3 , CaO , $(\text{C}_{14}\text{H}_6\text{O}_3)_3$, H_2O by Liechti and Suida⁽³⁾. Recently R. Mohlau⁽⁴⁾ gave the formula

(1) *Bull. Soc. Ind. Mulhouse*, 1875, 56.

(2) *Moniteur scientifique* 1883, 1086.

(3) *Mitt. d. Rechnol. Gew.-Museum, Wien*, **2** (1885), 26; **3** (1886), 5.

(4) *Ber.*, **46** (1913), 443.



moreover there are many other researches on the reaction-products of alizarin and alumina.

A few years ago, Bull and Adams studied the reaction of hydrochromic oxide or hydrous ferric oxide on sodium alizarate and concluded that in that case no true chemical compound was formed but adsorption compound. Williamson⁽¹⁾ researched the reaction between sodium alizarate and aluminium hydroxide. For this purpose he tried to determine the amount of sodium hydroxide, the by-product of the reaction, but could not get a reasonable datum, so he concluded that in this reaction no true aluminium alizarate is formed but an adsorption complex.

Now it is not too much to say that alizarin is almost insoluble in water at any condition, cold or hot, while it is easily soluble in the aqueous solution of sodium aluminate, giving a deep red colouration immediately, either cold or hot, and the author observed that if the former is added over a certain limit, its excess remains in state of yellow crystalline suspension in the coloured liquid and is easily visible under microscope. So the author thinks that some reaction might have occurred between these two compounds and it will be very interesting to research the reaction, since the reaction-product might be considered to have connection to Turkey-red from the point of view of the chemical constitution.

Experimental.

The Purification of Alizarin. The methods of the purification are proposed by many researchers. According to Graebe and Lieberman⁽²⁾ the sublimation process which Schutzenberger proposed is best applicable for alizarin. Lieberman⁽³⁾ dissolved alizarin in excess of a dilute sodium hydroxide solution and into the solution is passed carbon dioxide; then 2/3 part of the dyestuff is precipitated as acid sodium salt, while the co-existing isopurpurin remains in the solution. The precipitate of the acid salt is filtered and decomposed with hydrochloric acid. Schunk⁽⁴⁾ reported that

(1) *J. phy. Chem.* **28** (1924), 891.

(2) *Ann. Spl.*, **7** (1870), 301.

(3) *Ann.*, **183** (1876), 206.

(4) *Ann.*, **66** (1846), 187.

alizarin recrystallized from alcohol loses its crystalline water at 100°C. and sublimes by heating in a test-tube at 215°C. But afterwards he and Roemer⁽¹⁾ reported that alizarin begins to sublime at 110°C. and by continuous heating at ca. 140°C., and in this way it is able to purify from its homologues. Perkin⁽²⁾ gave some notice about the sublimation process. As to other methods of purification, alcohol and ether are generally used as solvents. Toluene is proposed by Liebermann⁽³⁾ to remove purpurin. Then the author, with the intention to know the best condition for purifying the raw alizarin, find that toluene is the best solvent and that even with toluene it is very difficult to get pure alizarin, although recrystallizations are repeated; so he modified the Liebermann's method as follows:—

Two grams of E. Merck's dry alizarin is dissolved in 2 litres of sodium hydroxide (ca. 1/20 N.) and filtered without suction, lest the glutinous solution causes to choke the filter paper. If the concentration of sodium hydroxide solution is too strong, the solution will become very slushy and take long time to filter, though the volume is small. Into the filtrate a current of carbon dioxide is slowly passed so long as almost of bubbles disappear. The dark red solution thus obtained is filtered off and the precipitate, acidic sodium alizarate, is neutralized with ca. 1 N. hydrochloric acid very slowly. This precipitate, normal alizarin, is filtered with Buchner's funnel and once more repeated the above treatment. Then the precipitate is washed with water until no trace of chlorine-ion is present and recrystallized twice with 250 c.c. of pure toluene. Thus purified alizarin melts at 286–288.5°C. and now it is boiled with 500 c.c. of saturated alum solution for about one hour in order to remove the residual homologues, filtered off while hot. This treatment is repeated twice more and once more recrystallized with 250 c.c. of toluene and at last with 300 c.c. of pure alcohol to remove a trace of toluene. After dried at 100°C., it melts at 288.5–289.5°C. (uncor.).

Analytical Study of the Product. On the quantitative estimation of alizarin, Knecht and Hibbert⁽⁴⁾ reported that the alcoholic solution of alizarin is reduced by the titanous trichloride. This is only one with regard to the method of estimation of alizarin; but this method is not applicable in this case. The author dissolved 0.0600 gr. of pure alizarin in 250 c.c. of toluene, i.e. 1/1000 mol solution.

(1) *Ber.*, **13** (1880), 41.

(2) *J. Soc. Chem. Ind.*, **14** (1895), 1026.

(3) *Ber.*, **35** (1902), 1781.

(4) *J. Soc. Dyers Col.*, **31** (1905), 241.

And an aqueous solution of sodium aluminate is stocked for about one month in order to settle the insoluble matter as much as possible, then the mol concentration, 0.0372 Al, is determined by Lunge's method.⁽¹⁾

These two solutions are poured into a well-stoppered bottle of a suitable capacity in a certain proportion and shaken for several hours at room temperature and then left to stand for a few hours. Now the supernatant toluene solution is pipetted out of the bottle and after adding certain volume of alkali, 1.16 N., compared with the standard alkali solution of alizarin colorimetrically, using Duboscq colorimeter.

The volumes of both reagents are recorded in Table 1. In this table, from A to G, each of them has too much amount of aluminate

Table 1.

No.	0.001-mol aliz. solution taken, in c.c.	Aluminate sol. taken		Colour of the upper layer after shakings.
		concentration in mol.	Volume in c.c.	
A	10	0.0372	10	colourless
B	5	0.0372	10	colourless
C	11	0.0372	10	colourless
D	10	0.0372	5	colourless
E	10	0.0372	1	colourless
F	10	0.0037	10	colourless
G	10	0.0037	5	colourless
H	10	0.0037	1	light yellow
I	10	0.00037	10	light yellow
J	10	0.00037	5	yellow
K	10	0.00037	1	yellow

for alizarin, because there is no alizarin remains in the upper layers. But in the last four (H~K), certain amount of alizarin remains in toluene even after shaking and the amount is determined by colorimetry, adding sodium hydroxide solution to obtain a bluish violet solution of sodium alizarate. These results are recorded in Table 2. Here, α -series, for example H α , means the upper layer, i. e. the toluene solution of alizarin after the reaction is completed. And β -series means the 1/1000 mol toluene solution of alizarin, viz. standard solution.

(1) *Z. angew. Chem.* **3** (1890), 227, 293.

Table 2.

No.	Toluene sol. of alizarin, taken in c.c.	1.16 N. NaOH solution, added in c.c.	Colorimeter reading in mm.			
			No. of measurement			Average value, magnified.
			1	2	3	
H _α	5	10	28.2	20.7	16.6	10000
H _β	2	10	3.0	1.9	1.4	942
I _α	5	10	24.3	15.6	20.1	10000
I _β	1	10	6.7	4.3	5.8	2800
J _α	5	10	12.4	8.1	17.2	10000
J _β	1	10	19.0	12.0	26.5	15182
K _α	2	10	9.8	7.9	6.6	10000
K _β	1	10	17.0	13.8	11.6	17464

Now, if the equal volumes of both α - and β -series are used, the numerical values of β -series, referred to $\alpha = 10000$ as the standard, are calculated as follows :

$$2 : 5 = X : 942,$$

$X = 377$ for H_β, if the equal volume as H_α taken. In this way above values are collected as shown in Table 3.

Table 3.

No.	Relative value	Comparing with the original solution, the conc. of alizarin diminished to
H _α	10000	377/10000
H _β	377	
I _α	10000	560/10000
I _β	560	
J _α	10000	3037/10000
J _β	3036	
K _α	10000	8732/10000
K _β	8732	

Hence, the fractions in Table 3 mean the values showing the free alizarin uncombined with aluminate. Table 4 represents those combined with aluminate.

Table 4.

No.	The fractional values that reacted with the sodium aluminate
H _α	$1 - (377/10000) = 9623/10000$
I _α	$1 - (560/10000) = 9440/10000$
J _α	$1 - (3036/10000) = 6964/10000$
K _α	$1 - (8732/10000) = 1268/10000$

Table 5 shows actual volumes of the 1/1000 mol solutions.

Table 5.

No.	Alizarin solution in c.c.	Aluminate solution in c.c.
H _α	9.62	3.72
I _α	9.44	3.72
J _α	6.96	1.86
K _α	1.27	0.37

From this table one can get easily the ratio in mol, the alizarin to the aluminate, as follows, Table 6.

Table 6

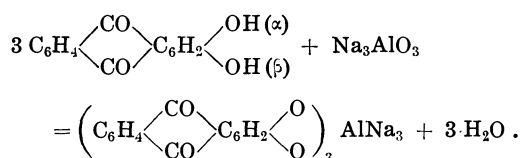
No.	Ratio in mol (Alizarin / Aluminate)	Average value
H _α	$962/372 = 2.6$	3.1
I _α	$944/372 = 2.5$	
J _α	$696/186 = 3.7$	
K _α	$127/37 = 3.4$	

From these experiments, it is clear that the reaction, which takes place between the alizarin and the sodium aluminate, is not a kind of adsorption but true chemical reaction. Of course, there are some colloidal particles coexist and therefore between these colloidal substances and the reaction-product, sodium aluminium alizarate, certain adsorption may occur. On the whole, the reactions between alizarin and sodium aluminate are two kinds, the one is true chemical and the other of an adsorption.

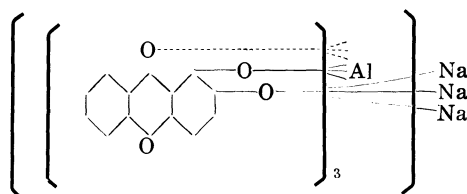
The author expresses his hearty thanks to Prof. Dr. J. Inouye for the kind help in carrying out this research.

Summary.

1. The method of purification of alizarin is proposed.
2. A deep orange, hydrophile colloidal substance is produced when alizarin is added into an aqueous solution of sodium aluminate. The mechanism of the reaction may be as follows ;



And the constitutional formula will be



Laboratory of Applied Chemistry, Technical Faculty,
Tohoku Imperial University, Sendai.

October, 1926.

THE RATE OF OXIDATION OF STANNOUS SALT BY
OXYGEN AND THE ELECTRICAL CONDUCTIVITY
OF MIXTURES OF SULPHURIC ACID
AND STANNOUS SULPHATE.

By Susumu MIYAMOTO.

Received November 16th, 1931. Published February 28th, 1932.

Introduction.

The effect of the positive and negative catalytic actions of a number of substances on the rate of oxidation of stannous chloride solution had been studied by S. W. Young.⁽¹⁾ The rate of oxidation of the same substances by passing air-bubbles was also studied by the present writer a few

(1) *J. Am. Chem. Soc.*, **23** (1901), 119 and 450.

years ago, and the effect of substances such as sodium hydroxide, sodium carbonate, hydrochloric acid and sulphuric acid on the rate of oxidation of stannous salt was observed.

The experimental procedure was as follows.

Air, washed by acidified potassium bichromate solution and sodium hydroxide solution, was passed into the reacting solution, contained in a large test-tube (diameter = 3 cm.), through a glass tube of definite diameter at a constant velocity. After t -minutes the air current was stopped and the total amount of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back with sodium thiosulphate solution of known concentration. The measurements were carried out in an ordinary water-thermostat. The amount of reacting solution was made up to 40 c.c. in each case, and the exit tube was kept at a fixed depth below the surface of the reacting solution.

(1) **The Effect of Sodium Hydroxide.**⁽¹⁾ As will be seen in Fig. 1, the relation between the rate of oxidation of stannous hydroxide and the concentration of sodium hydroxide solution can be shown graphically by a two-stage curve.

The rate of oxidation of stannous hydroxide increases rapidly with the increase of concentration of sodium hydroxide as far as it attains a maximum value, when the concentration of sodium hydroxide is about 0.18 normal. Further increases of the concentration of sodium hydroxide cause a gradual decrease on the rate of oxidation of stannous hydroxide.

(2) **The Effect of Sodium Carbonate.**⁽²⁾ Contrary to expectation, stannous hydroxide oxidizes at an extremely slow rate in sodium carbonate solution, and the increase of concentration of sodium carbonate has nearly no effect upon the rate of oxidation of stannous hydroxide, as will be seen in Fig. 1.

(3) **The Effect of Hydrochloric Acid.**⁽³⁾ The effect of hydrochloric acid on the rate of oxidation of stannous chloride was found to be analogous to that of sodium hydroxide on the rate of oxidation of stannous hydroxide. The effect again can be illustrated by a two-stage curve. The rate of oxidation of stannous chloride increases rapidly with the increase of the concentration of hydrochloric acid, as far as the concentration of the latter reaches about 0.25 normal. In the more concentrated solution of hydrochloric acid

(1) Miyamoto, this Bulletin, **2** (1927), 155.

(2) Ibid., **3** (1928), 43.

(3) Ibid., **2** (1927), 259.

the rate of oxidation of stannous chloride is independent of its concentration, and the increase of concentration of hydrochloric acid has but little effect upon the rate of oxidation.

(4) **The Effect of Sulphuric Acid.**⁽¹⁾ The influence of sulphuric acid is quite analogous to that of hydrochloric acid, as will be seen in Fig. 1. The rate of oxidation increases with the increase of the concentration of sulphuric acid as far as the concentration of the latter attains the value of about 0.8 normal. Further increases of the concentration of sulphuric acid have only a slight effect upon the rate of oxidation of stannous salt.

The observed values of the rate of oxidation of stannous salt solution by air in the presence of the above mentioned acid or alkali were already published in the previous papers.⁽²⁾ The representative values are summarized in Table 1, in which $\frac{\Delta v}{\Delta t}$ means the volume of sodium thiosulphate

Table 1.

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

C_{NaOH} normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.	$C_{\text{Na}_2\text{CO}_3}$ normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.	C_{HCl} normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.	$C_{\text{H}_2\text{SO}_4}$ normal.	$\frac{\Delta v}{\Delta t}$ c.c./min.
0.00595	0.0224	0.0155	0.00600	0.00647	0.0170	0.01410	0.0304
0.02170	0.0531	0.1655	0.00766	0.09672	0.0227	0.2959	0.0339
0.04057	0.0893	0.4655	0.00689	0.1682	0.0657	0.7185	0.0710
0.1081	0.230	0.8405	0.00660	0.3235	0.106	0.8370	0.115
0.1706	0.257	1.216	0.00585	0.4587	0.118	0.970	0.121
0.2204	0.259			0.8151	0.118	1.377	0.117
0.3252	0.246			1.360	0.115	1.396	0.127
0.5500	0.215			1.811	0.132	1.423	0.123
1.130	0.168			2.262	0.139	2.052	0.109
1.704	0.126					2.558	0.107
2.312	0.0998					2.727	0.105
						2.832	0.108

solution of 0.0996 normal, equivalent to the quantity of stannous salt oxidized per minute under the conditions described in the previous paper.⁽²⁾

The above mentioned substances, with the exception of sodium carbonate, have thus similar influence upon the rate of oxidation of stannous

(1) Miyamoto, this Bulletin, 4 (1929), 48.

(2) Loc. cit.

salt. The effect of each of them is illustrated by a two-stage curve in Fig. 1. At low concentrations of the alkali or the acid, the rate of oxidation of stannous salt increases rapidly as the concentration of the alkali or the acid increases.

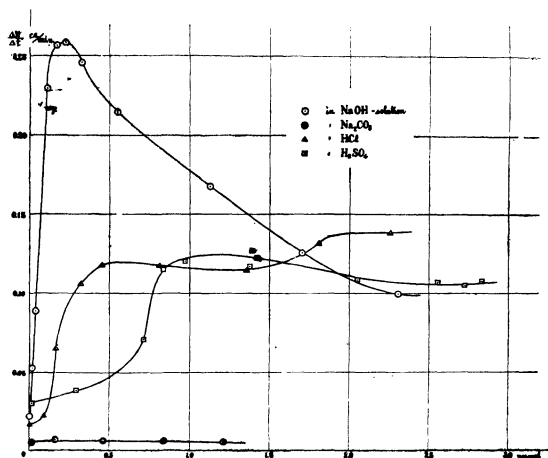


Fig. 1.

At high concentrations of the alkali or the acid, the rate of oxidation of stannous salt is not much influenced by the increase of concentration of these substances, and it was also confirmed, that in this region the rate of oxidation is independent of the concentration of stannous salt. The present writer explained the phenomenon by the assumption⁽¹⁾ that the rate of oxidation, observed in this region, is not the characteristic value of stannous salt, but is equivalent to the rate of solution of oxygen into alkaline or acidic solution, free from oxygen. This assumption is very probable as was discussed in the previous papers,⁽²⁾ and it will be of no use to repeat the discussion of the assumption, proposed to interpret the mechanism of this part.

This paper is intended to interpret why the rate of oxidation of stannous salt solution by oxygen increases with the increase of concentration of sodium hydroxide, hydrochloric acid or sulphuric acid in the initial stage. The following assumptions are proposed by the present writer to interpret the phenomenon.

(1) Miyamoto, this Bulletin, **3** (1928), 98.

(2) Loc. cit.

Stannous ion is oxidized by oxygen at an extremely slow rate, and the formation of some complex ion, containing the tin atom, causes the rapid increase in the rate of oxidation of stannous salt. This assumption will be very probable as will be discussed in the following. It is a well known fact that stannous hydroxide, precipitated from stannous salt solution by the addition of sodium hydroxide, dissolves in the excess of sodium hydroxide, forming a complex compound, sodium stannite. If we apply the assumption, above described, in this case, stannous hydroxide is oxidized at an extremely slow rate, while sodium stannite, the concentration of which increases with the increase of concentration of sodium hydroxide, is oxidized rapidly.

Then the experimental fact is clearly interpreted as follows. The rate of oxidation of stannous hydroxide increases with the increase of concentration of sodium hydroxide, as a result of the formation of stannite, as far as it attains the maximum rate of solution of oxygen into sodium hydroxide solution. The decrease of the rate of oxidation of stannous hydroxide with the further increase of concentration of sodium hydroxide at the second stage takes place from quite a different cause. It is due to the decrease of the maximum rate of solution of oxygen into sodium hydroxide solution with the increase of concentration of sodium hydroxide, according to the opinion of the present writer.

The experimental fact, that stannous hydroxide is oxidized at a very slow rate in sodium carbonate solution, in which a minute quantity of stannite is formed, is another fact favourable for the present theory. It was experimentally confirmed,⁽¹⁾ that oxygen dissolves into sodium carbonate solution at nearly the same rate as into sodium hydroxide solution, and it can be described that the slow rate of oxidation of stannous hydroxide in sodium carbonate solution has no relation to the rate of solution of oxygen into the solution.

The above described assumption can quite similarly be applied for the interpretation of the effect of hydrochloric acid. By the measurement of electrical conductivity of the mixture of stannous chloride and hydrochloric acid solution, S. W. Young⁽²⁾ confirmed that at least two complex compounds, such as hydrotrichlorostannous acid HSnCl_3 and hydrotetrachlorostannous acid H_2SnCl_4 are formed in the hydrochloric acid solution of stannous chloride.

Then the influence of the increase of concentration of hydrochloric acid on the rate of oxidation of stannous chloride can be interpreted in the same

(1) Miyamoto, this Bulletin, **3** (1928), 76.

(2) *J. Am. Chem. Soc.*, **23** (1901), 21.

manner as in the previous case by the assumptions that stannous chloride itself oxidized at an extremely slow rate, and that the formation of complex acids, whose concentrations increase with the increase of concentration of hydrochloric acid, is the cause of the increase of the rate of oxidation of stannous chloride.

From the result of the study of the effect of sulphuric acid on the rate of oxidation of stannous salt solution, it can be expected that some complex compound will be formed in the mixture of stannous sulphate and sulphuric acid solution, if the assumption, above described, be acceptable. In other words, the effect of sulphuric acid on the rate of oxidation of stannous salt can be interpreted in the same way as in the previous cases, if the formation of some complex compound in sulphuric acid solution of stannous salt be experimentally confirmed.

The measurement of electrical conductivity of the solution will be one of the suitable methods to ascertain whether the combination of stannous sulphate and sulphuric acid takes place in the solution, and the following experiment was carried out for this purpose.

Experimental.

Sulphuric acid, Kahlbaum for analysis, was employed. Stannous sulphate was prepared by the method of C. M. Carson⁽¹⁾ from copper sulphate, Kahlbaum for analysis, tin, Kahlbaum for analysis, and sulphuric acid. The white crystals of pure stannous sulphate were easily obtained by this method in the laboratory.

The conductivity cell of a suitable type for the present purpose, shown graphically in Fig. 2, was manufactured in the laboratory with hard glass. Its cell constant is about 30. The experimental procedure was the ordinary Wheatstone bridge method, slide wire bridge of 2000 division and precision decade resistance box, manufactured and examined by Ando Co., being employed. The cell constant of the conductivity vessel was determined by measuring the conductance of potassium chloride solution as usual. It is not necessary to use conductivity water of a high degree of purity for the present purpose. Distilled water from tin vessel, freed from carbon dioxide by drawing a current of air, free from carbon dioxide, through the water, was employed. The measurements were carried out in an electrically heated and controlled water thermostat, whose temperature was kept constant within fluctuations of less than 0.03°C.

(1) *J. Am. Chem. Soc.*, **48** (1926), 906.

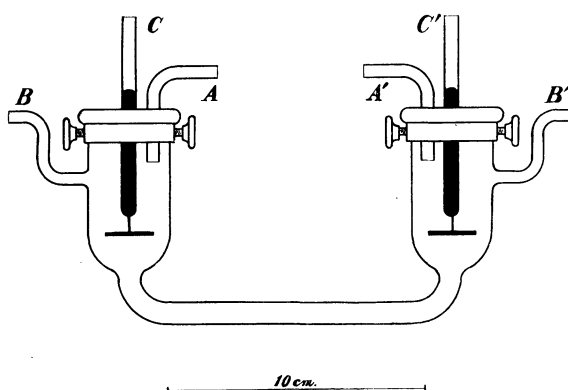


Fig. 2.

As stannous sulphate in sulphuric acid solution is oxidized by air, the preparation of the solution and the measurement of conductivity were carried out in the atmosphere of nitrogen as follows. The measured quantity of stannous sulphate crystals was placed in an Erlenmeyer flask, and when the air in the flask had been replaced by nitrogen, a definite quantity of sulphuric acid solution of known concentration was poured into the flask. The air in the conductivity cell was also entirely replaced by nitrogen, before the solution was poured into the cell, and during the observation, nitrogen gas was passed continuously in the cell through A and A' (Fig. 2) to prevent the oxidation of stannous sulphate. The specific conductance of pure sulphuric acid solution was also observed, although it is given in Landolt-Börnstein Tabellen.

The results, observed at 18°C. and at 25°C., are given in Tables 2 and 3 respectively. They are shown graphically in Fig. 3. In the Tables, K means the specific conductance of the mixture, ΔK the difference of specific conductance of the mixture and that of pure sulphuric acid solution.

Discussion.

As was expected, the influence of stannous sulphate on the specific conductance of sulphuric acid solution was confirmed to be similar to that of stannous chloride on the specific conductance of hydrochloric acid solution, which had been studied by S. W. Young.⁽¹⁾ When the concentration of sulphuric acid is less than about 0.6 normal, the specific conductance

(1) Loc. cit.

Table 2.

Temp. = 18°C.

$C_{H_2SO_4}$ normal.	C_{SnSO_4} normal.	K	ΔK	$\frac{\Delta K}{C_{SnSO_4}}$
0.2596	0	0.05564	0	0
	0.2000	0.05690	+0.00126	+0.00630
	0.4000	0.05874	+0.00310	+0.00775
	0.6000	0.06099	+0.00535	+0.00892
	1.000	0.06631	+0.01067	+0.01067
0.5330	0	0.1091	0	0
	0.4012	0.1098	+0.0007	+0.0017
	0.6007	0.1107	+0.0016	+0.0027
	1.001	0.1130	+0.0039	+0.0039
1.066	0	0.2093	0	0
	0.1998	0.2073	-0.0020	-0.0100
	0.4001	0.2055	-0.0038	-0.0095
	0.6000	0.2039	-0.0054	-0.0090
	0.9998	0.2000	-0.0093	-0.0093
1.853	0	0.3423	0	0
	0.4012	0.3304	-0.0119	-0.0297
	0.6000	0.3266	-0.0157	-0.0262
	1.004	0.3166	-0.0257	-0.0256
3.044	0	0.5056	0	0
	0.4000	0.4860	-0.0196	-0.0490
	0.6002	0.4737	-0.0319	-0.0532
	1.000	0.4573	-0.0483	-0.0483
3.706	0	0.5762	0	0
	0.1998	0.5636	-0.0126	-0.0630
	0.4000	0.5507	-0.0255	-0.0638
	0.5999	0.5388	-0.0374	-0.0623
	1.000	0.5155	-0.0607	-0.0607
6.088	0	0.7198	0	0
	0.1999	0.7009	-0.0189	-0.0945
	0.3004	0.6913	-0.0285	-0.0950
	0.4000	0.6823	-0.0375	-0.0938

Table 3.

Temp. = 25°C.

$C_{H_2SO_4}$ normal.	C_{SnSO_4} normal.	K	ΔK	$\frac{\Delta K}{C_{SnSO_4}}$
0.2591	0	0.05977	0	0
	0.1999	0.06141	+0.00164	+0.0082
	0.4001	0.06329	+0.00352	+0.0088
	0.6000	0.06605	+0.00628	+0.0105
	0.8000	0.06898	+0.00921	+0.0115
	1.000	0.07208	+0.01231	+0.0123
	1.200	0.07533	+0.01556	+0.0130
0.5320	0	0.1180	0	0
	0.3999	0.1187	+0.0007	+0.0018
	0.6000	0.1196	+0.0016	+0.0027
1.064	0	0.2266	0	0
	0.2000	0.2242	-0.0024	-0.0120
	0.3999	0.2224	-0.0042	-0.0105
	0.6001	0.2207	-0.0059	-0.0098
	1.000	0.2180	-0.0086	-0.0086
	1.400	0.2156	-0.0110	-0.0079
1.850	0	0.3718	0	0
	0.4000	0.3604	-0.0114	-0.0285
	0.6000	0.3552	-0.0166	-0.0277
2.431	0	0.4656	0	0
	0.2000	0.4581	-0.0075	-0.0375
	0.4000	0.4501	-0.0155	-0.0388
	0.6002	0.4420	-0.0236	-0.0393
	1.000	0.4271	-0.0385	-0.0385
3.034	0	0.5535	0	0
	0.4000	0.5323	-0.0212	-0.0530
	0.6001	0.5216	-0.0319	-0.0532
3.701	0	0.6319	0	0
	0.2000	0.6185	-0.0134	-0.0670
	0.4000	0.6055	-0.0264	-0.0660
	0.6000	0.5928	-0.0391	-0.0652
	1.000	0.5783	-0.0636	-0.0636
6.068	0	0.7983	0	0
	0.2000	0.7783	-0.0200	-0.1000
	0.2999	0.7685	-0.0298	-0.0993
	0.4000	0.7587	-0.0396	-0.0990

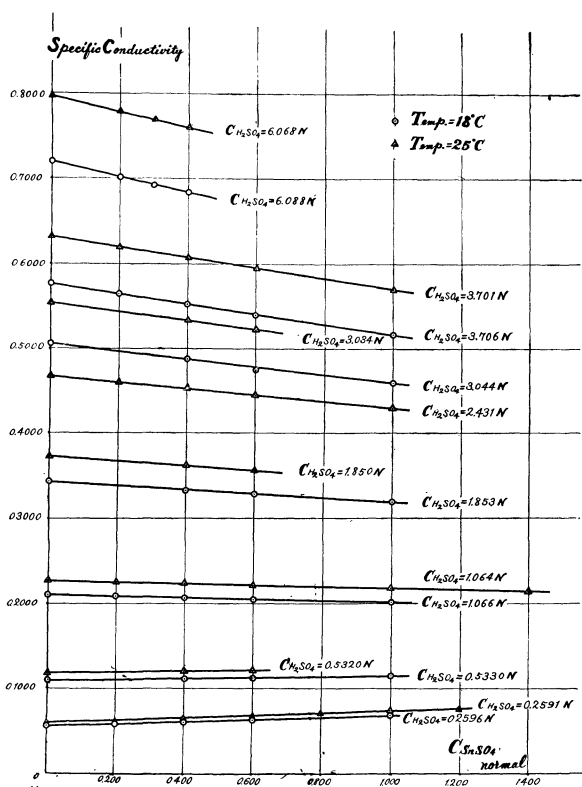


Fig. 3.

of the mixture increases gradually with the increase of concentration of stannous sulphate. The addition of stannous sulphate into sulphuric acid solution of proper concentration (approximately 0.7 normal) will have no effect on the specific conductance of the solution. When the concentration of sulphuric acid is greater than about 1 normal, the specific conductance of the mixture decreases with the increase of concentration of stannous sulphate. The decrease of the specific conductance of the solution, caused by the addition of stannous sulphate is considerably great, and it will be unable to be interpreted as the effect of common ion. The formation of some complex compound will be evident.

The relation between the percentage influence, $\left(\frac{\Delta K}{K}\right) \div \left(\frac{K}{C_{SnSO_4}}\right)$, and the concentration of sulphuric acid, can be calculated from the results, given in Tables 2 and 3. The calculated values, when the concentration of stannous sulphate is about 0.4 normal, are shown in Table 4, and graphically in Fig. 4. As will be seen in the figure, the curve does not show a

Table 4.

Temp.	$C_{H_2SO_4}$	K $C_{SnSO_4}=0$	K $C_{SnSO_4}=0.4000$	$\frac{\Delta K}{C_{SnSO_4}}$	$\left(\frac{\Delta K}{C_{SnSO_4}}\right) \div \left(\frac{K}{C_{SnSO_4}=0}\right)$
18°C.	0.2596	0.05564	0.05874	+0.00775	+0.139
	0.5330	0.1091	0.1098	+0.0017	+0.0156
	1.066	0.2093	0.2055	-0.0095	-0.0454
	1.853	0.3423	0.3304	-0.0297	-0.0868
	3.044	0.5056	0.4860	-0.0490	-0.0969
	3.706	0.5762	0.5507	-0.0638	-0.1107
25°C.	6.088	0.7198	0.6823	-0.0938	-0.130
	0.2591	0.05977	0.06329	+0.0088	+0.147
	0.5320	0.1180	0.1187	+0.0018	+0.0153
	1.064	0.2266	0.2224	-0.0105	-0.0463
	1.850	0.3718	0.3604	-0.0285	-0.0767
	2.431	0.4656	0.4501	-0.0388	-0.0833
	3.034	0.5535	0.5323	-0.0530	-0.0958
	3.701	0.6319	0.6055	-0.0660	-0.1044
	6.068	0.7983	0.7587	-0.0990	-0.1240

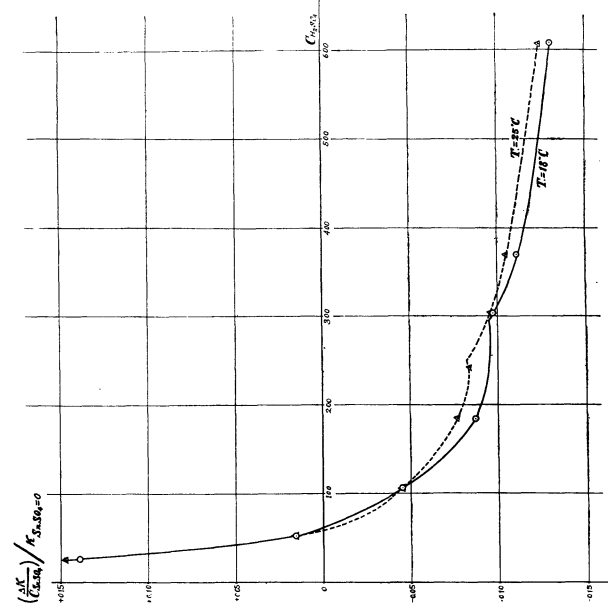
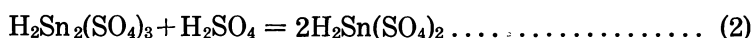
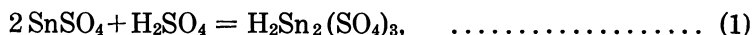


Fig. 4.

maximum or a minimum, but it has a turning point at about 3 normal when the temperature is 18°C., and at about 2.5 normal when the temperature is 25°C. In other words, the graph which represents the relation between the percentage influence and the concentration of sulphuric acid solution is composed of two curves.

For the interpretation of the result, it will be necessary to assume the formation of two kinds of molecular complexes, quite the same way as in the case of stannous chloride solution containing excess of hydrochloric acid.⁽¹⁾ It is highly probable that compounds are formed in the solution, with molecular complexes of the type shown in the following reactions.



The potassium salts of these complex acids, $\text{K}_2\text{Sn}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Sn}(\text{SO}_4)_2$, had been found by Marignac.⁽²⁾ The assumption, that at low concentrations of sulphuric acid solution the equilibrium of the first reaction (1) predominates, and at high concentrations the equilibrium of the second reaction (2) becomes noticeable, will be sufficient to interpret the observed phenomenon clearly.

Thus the assumption that the rate of oxidation of stannous salt itself by oxygen is extremely small, and the formation of some molecular complexes causes the increase of the rate of oxidation of stannous salt solution will be applied for the interpretation of the rate of oxidation of stannous salt containing sulphuric acid also. This assumption will generally be applied for the interpretation of the rate of oxidation of stannous salt in the presence of a large quantity of other substances.

When the solvent is not water, the mechanism of the oxidation will be different, and the assumption, above described, will not be satisfied. For example, it was confirmed in the laboratory of the present writer by a preliminary experiment, that the alcoholic solution of anhydrous stannous chloride is oxidized by oxygen at a considerably rapid rate.

The assumption, which attributes the increase of the rate of oxidation of stannous salt solution with the increase of concentrations of acid or alkali to the catalytic action of the acid or the alkali, will not be justifiable. Stannous salt is oxidized rapidly in sodium hydroxide solution, while it is oxidized at an extremely slow rate in sodium carbonate solution, in which Na- and OH- ions are also present.

(1) Loc. cit.

(2) Mellor: Treatise on Inorganic and Theoretical Chemistry, Vol. VII, p. 478.

The writer expresses his thanks to Messrs. T. Kaya, T. Nogami and S. Tanaka for their assistance during the course of this research, and the writer is indebted to the Department of Education for a grant.

Summary.

(1) The effects of sodium hydroxide, sodium carbonate, hydrochloric acid and sulphuric acid on the rate of oxidation of stannous salt solution by air were described.

(2) The specific conductance of sulphuric acid solution containing stannous sulphate was observed. When the concentration of sulphuric acid is less than about 0.6 normal, specific conductance of the mixture increases with the increase of concentration of stannous sulphate and when the concentration of sulphuric acid is greater than about 1 normal, the specific conductance of the mixture decreases with the increase of concentration of stannous sulphate. The assumption, that two kinds of molecular complexes are formed in the solution, was proposed for the interpretation of the result, and as the most probable molecular complexes, $\text{H}_2\text{Sn}_2(\text{SO}_4)_3$ and $\text{H}_2\text{Sn}(\text{SO}_4)_2$ were mentioned.

(3) The assumptions, that the rate of oxidation of stannous salt itself by oxygen is extremely small, and that the rate of oxidation increases as a result of the formation of some complex compounds in the solution, were proposed. The assumptions were applied for the interpretation of the effect of sodium hydroxide, sodium carbonate, hydrochloric acid and sulphuric acid on the rate of oxidation of stannous salt solution by air.

Laboratory of Physical Chemistry,
Hiroshima University, Hiroshima.

DAS VERHALTEN DER PYRIDINGRUPPE BEI DER ELEKTROCHEMISCHEN OXYDATION.

II. PICOLIN.

Von Moriaki YOKOYAMA.

Eingegangen am 31. December 1931. Ausgegeben am 28. März 1932.

Es ist schon bei Gelegenheit der Schilderung der elektrochemischen Oxydation des Pyridins darauf hingewiesen worden, wie das Verhalten des gegen starke Oxydationsmittel sehr widerstandsfähigen Pyridins gegen anodischen Sauerstoff ist.⁽¹⁾ Davon haben wir neue Beweise erhalten, als wir die elektrochemische Oxydation beim Picolin anzuwenden suchten.

Friedrich Fichter und seine Schüler⁽²⁾ hatten bei der elektrochemischen Oxydation von Toluol, das in seiner Stellung zum Benzol dem Picolin in der Pyridinreihe entspricht, am Benzolkern hydroxylierte Produkte neben Benzoesäure erhalten. Dass der Pyridinkern in seinem chemischen Verhalten gegen Oxydationsmittel durch grössere Beständigkeit als der Benzolkern ausgezeichnet ist, ist wiederholt festgestellt worden. So war es eine interessante Aufgabe zu studieren, ob das Picolin ebenso wie Benzolkerne bei Einwirkung von anodischen Sauerstoff zu den entsprechenden Oxyderivaten oxydiert wird.

Beschreibung der Versuche.

Eine Lösung von 3.8 gr. Picolin (Kahlbaum) in 100 cm³ 2-n Schwefelsäure wurde in der Tonzelle an einer zylindrischen Bleianode (mit vorher frisch hergestelltem Bleidioxid-Ueberzug) mit 0.05 Amp/cm² unter starker Rührung elektro-oxydiert. Die Temperatur wurde auf ca. 20° gehalten. Die Kathode, ein Platinblech in 2-n Schwefelsäure, umgab die Tonzelle. Die Strommenge (ber. für die Ueberführung von 1 gr. C₆H₇N in C₆H₅O₂N zu 1.75 Amp-Std.) betrug 10 Amp-Std.; die Stromausbeute war ungefähr 40%.

Während der Elektrolyse trat keine Färbung des Anolyten⁽³⁾ ein. In einigen Stunden nach beendeter Elektrolyse nimmt jedoch der Elektrolyt eine violettbraune Farbe an, und dann fällt eine violettbraunen Niederschlag aus. Während der Elektrolyse entweicht reichlich Kohlendioxid, das stets durch einen Kaliapparat abgesaugt wurde; das Gewicht des CO₂ war jeweils ca. 0.95 gr.

(1) Yokoyama u. Yamamoto, Dieses Bulletin, **7** (1932), 28.

(2) *Z. Elektrochem.*, **19** (1931), 781.

(3) Aber bei höherer Temperatur (70°~80°C.) kann man die Entstehung einer bräunlichen Färbung beobachten.

(4) Diesen konnten wir bis heute noch nicht untersuchen.

A. Die in Aether leicht löslichen Produkte ; Nach der Filtration des violettgefärbten Substanz wurde der Anolyt zunächst mit Aether mehrmals ausgeschüttelt. Nach Verdunsten der ätherischen Lösung entstand ein blaugefärbtes Harz, welches kleine Mengen von Ameisensäure und Essigsäure, aber keine Oxalsäure erhielt.

B. Die mit Wasserdampf flüchtigen Produkte: Die mit Aether extrahierte Lösung des Anolyten wurde hierauf mit Bariumcarbonat gegen Lackmus zwecks Entfernung der Schwefelsäure neutralisiert.

Das Filtrat vom Bariumsulfat wurde im Wasserdampfstrom langsam destilliert, bis das Destillat gegen Nesslerisches Reagenz und gegen fuchsin-schweflige Lösung nicht mehr reagierte ; die Vorlage enthielt zwecks Aufnahme des flüchtigen Gases etwa 100 cm³ Wasser.

Das farblose Destillat gibt die allgemeinen Carbonylreaktionen; in salzsaurer Lösung bildet sie das orangegelbe Hydrazon, dessen Schmelzpunkt bei 173°C. liegt ; mit ammoniakalischer Silberlösung erscheint beim schwachen Erwärmen ein prächtigen Silberspiegel und aus Fehlingscher Lösung wird Cu₂O abgeschieden.

Nach den Eigenschaften der reinen Substanz handelt es sich um den von G. Lénárt⁽¹⁾ beschriebenen Pyridylaldehyd. Ausserdem lässt sich Ammoniak und unverändertes Picolin nachweisen.

C. Die mit Wasserdampf nicht flüchtigen Produkte : Der etwas bräunlich gefärbte Rückstand der Wasserdampfdestillation wird bis zur Syrupkonsistenz eingeeengt und dann bei einer Temperature von 70°C. mit einer gesättigten Lösung von Kupferacetat versetzt. Es fallen sofort schöne, metallglänzende, violett gefärbte Blättchen und Nadeln aus, die nach dem Erkalten abfiltriert und gewaschen werden. Dann wird die Kupferverbindung mit Schwefelwasserstoff in der Siedehitze zersetzt.

Nachdem alles Salz zersetzt ist, trägt man Tierkohle ein und kocht. Aus dem Filtrat erhält man nach dem Erkalten Pikolinsäure in fast farblosen, feinen Nadeln (= 1.1 gr.), die nach der Umkrystallisation aus Wasser bei 135°C. schmelzen. Das Kupfersalz wird bei 110°C. getrocknet und der Analyse unterworfen.

Subst. = 0.1854, 0.1664 ; CuO = 0.0473, 0.0424 gr. Gef.: Cu = 20.39, 20.35%.
Ber. für (C₆H₄O₂N)₂Cu: Cu = 20.62%

Nach dem Filtrieren des Schwefelkupfers und dem Abdampfen der frei gewordenen Essigsäure im Vakuum entsteht eine sehr kleine Menge eines bräunlich gefärbten und etwas hygroskopischen Harzes. Es besteht aus

(1) *Ber.*, **47** (1914), 808 ; vgl. Harries und Lénárt, *Ann.*, **410** (1915), 96, 115.

einer Substanz (Pikolilalkin),⁽¹⁾ welche ein Platinsalz liefert, das bei 168°–175°C. unter Schäumen schmilzt. Das Produkt könnte dadurch entstanden sein, dass der beim Abbau unter anderem entstehende Formaldehyd mit noch unangegriffenem Pikolin unter Einwirkung der Stromwärme an der Anode sich kondensiert. Ausserdem konnten wir Spuren von Salpetersäure nachweisen.

Wir untersuchten auch die Elektrolyse an Platinanoden, welche ganz analog, aber unter sehr niedriger Stromausbeute verläuft. Der grösste Teil des Ausgangsmaterial bleibt unverändert.

Unsere eingangs geäusserte Ansicht, dass die Bildung hydroxylierter Derivate möglich sei, hat sich bisher nicht bestätigt.

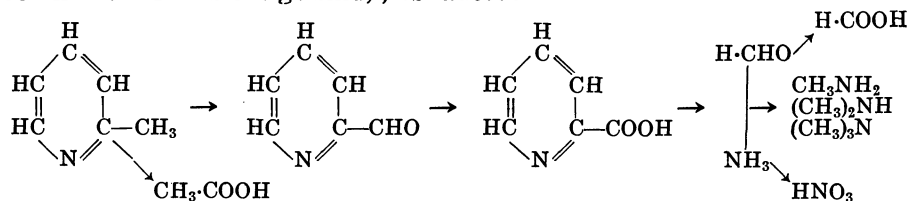
Elektrochemische Oxydation von Picolinsäure.

Da nach obigen Versuchen anzunehmen ist, dass die Abbauprodukte durch weitere Oxydation der Picolinsäure entstanden sind, so haben wir diese Säure zur Kontrolle oxydiert. Die Apparatur und die Elektrolysebedingungen waren dem Vorigen analog.

2.2 gr. Picolinsäure (gereinigt durch mehrmalige Umkrystallisation aus Wasser) wurden in 100 ccm 2-n Schwefelsäure gelöst, und bei 20°C. an einer Bleidioxydanode mit der anodischen Stromdichte 0.05 Amp./ cm² oxydiert; die Kathode war ein Platinblech, der Katholyt 2-n Schwefelsäure.

Während der Elektrolyse entwichen CO₂ (= 0.6 gr.) und CO. Nach der Elektrolyse behandelten wir den Anolyt in der oben geschilderten Weise und erhielten folgende Produkte: 0.3 gr. Ameisensäure, 0.03 gr. Ammoniak als Salmiak, und kleine Mengen von Mono-, Di- und Trimethylamin, welche, wie in einer frühen Arbeit⁽²⁾ berichtet wurde, durch Kondensation des beim Abbau der Säure gebildeten Formaldehyds mit Ammoniumsulfat entstanden war.

Unter Zusammenfassung aller bisherigen Beobachtungen kann man einstweilen ein Schema für die elektrochemische Oxydation des Picolins aufstellen, (wobei die letzten Stufen Kohlendioxyd und Kohlenmonoxyd noch nicht berücksichtigt sind); es lautet:



(1) Ladenburg, *Ber.* **22** (1889), 2583.

(2) Dieses Bulletin, **7** (1932), 28.

Herrn Kazuo Yamato sei an dieser Stelle für ihre bei dieser Arbeit geleistete Hilfe bestens gedankt.

Zusammenfassung.

(1) Bei der elektrochemischen Oxydation von Picolin an der Bleidioxyd-anode in verdünnter Schwefelsäure wurden die folgenden Oxydationsprodukte erhalten: eine grosse Menge von Picolinsäure, kleinere Mengen von Ameisensäure, Essigsäure, Ammoniak, Salpetersäure, Picolilalkin, Kohlenmonoxyd und Kohlendioxyd.

(2) Pikolinsäure wurde bei den gleichen Bedingungen wie bei der Oxydation von Picolin elektro-oxydiert, und ergab auch Ameisensäure, Ammoniak und Formaldehyd, welches letzteres durch sofortige Kondensation mit Ammoniak Methylamin und seine Verwandten bildete.

Dadurch wurden die Beziehungen zwischen Picolin und seinen Abbauprodukten bei der elektrochemischen Oxydation aufgeklärt.

Yokohama Technische Hochschule, Yokohama.

MESSUNG DER DIFFUSIONSKONSTANTE.⁽¹⁾

Von Yusiti NISIZAWA.

Eingegangen am 16. December 1931. Ausgegeben am 28. März 1932.

Die Viskosität einer Nitrozelluloselösung ist je nach den angewandten Baumwollenmaterial oder nach dem Herstellungsverfahren verschieden, und man kann annehmen, daß die Größe des Baumwollenmolekels hierbei in Frage käme. Es gibt auch andere Theorien, nach denen zwischen Viskosität der Lösung und Größe der Moleküle keine Parallele in einem solchen einfachen Verhältnis besteht, oder in denen man die Unabhängigkeit zweier Eigenschaften annimmt.

Im allgemeinen aber wird folgendes Verhältnis angenommen :

$$\eta_s = \eta_M \left\{ 1 + 2.5 \varphi \left[1 + \frac{1}{\lambda \eta_M r^2} \left(\frac{D\zeta}{2\pi} \right)^2 \right] \right\}$$

λ = relative Leitfähigkeit, D = Dielektrizitäts-Konstante, ζ = elektrokinetische Potentialdifferenz, r = Radius des Moleküls.

Obwohl die Veränderung der Viskosität nicht durch den Dispersionsgrad der Baumwollmoleküle erklärt werden kann, muß es für technische Zwecke, beim Klopff- und Knetverfahren der Baumwollbereitung u. dgl. einen Vorteil geben, den Dispersionszustand der Nitrozellulosenmoleküle

(1) J. Chem. Soc. Japan, **50** (1929), 391.

usw. festzustellen. Außerdem ist es nicht ausgeschlossen, daß bei Zersetzung der Nitrozellulose durch Bestrahlung eine Dispersion der Moleküle vorkommen kann. Um dies klarzustellen, habe ich versucht, für die Messung der Größe der Nitrozellulosenmolekülen eine Methode auszubauen.

Für die Messung eines Teilchens von einem Molekül, besonders bei Kolloidalen Substanzen, gibt es eine direkte Methode, die mit Hilfe von Ultramikroskop oder -filter die Größe eines Teilchens oder Moleküls ablesen kann, und eine indirekte, die durch Sedimentation, oder besser durch Diffusion ihre Größe feststellen kann. Es ist bekannt, daß bei Messung von Nitrozellulosenkolloiden die beiden ersten Methoden nicht angewandt werden können und man muß daher eine von den beiden letzteren zur Anwendung bringen. In Wirklichkeit aber gibt es keine besondere Methode außer der Diffusionsmethode, die zu dieser Untersuchung benutzt werden kann.

Zur Messung der Diffusionsgeschwindigkeit ist es nötig, die Konzentration einer Probe wiederholt festzustellen. Dafür gibt es zwar eine colorimetrische Methode und die Messung des Brechungsexponentes, usw. Bei der Messung der Konzentration von Nitrozellulosenkolloid kann man diese Methoden aber nicht anwenden; und es ist vorteilhaft, jedesmal eine bestimmte Lösungsmenge herauszunehmen und ihre Konzentration direkt zu bestimmen. Dies ist also der Grund, daß man im allgemeinen bei der Messung der Diffusionsgeschwindigkeit von Nitrozellulose in wiederholten Proben die darin gelöste Menge von Nitrozellulose feststellt.

Wenn man beim Entnehmen einer Probe das Gefäß von oben öffnet, so tritt in der oberen Schicht der Lösung eine Temperaturabnahme durch Verdunstung oder durch direkte Wärmeabgabe an die Luft ein, und es besteht die Gefahr, daß der Diffusionszustand durch die dabei entstandene Gegenströmung zerstört wird. Obwohl man dabei die Probe von der Seite des Gefäßes entnimmt, so wird dennoch diese Gefahr nicht leicht beseitigt.

Um eine solche Gefahr, die bei der Messung der Diffusionsgeschwindigkeit des Kolloides, wie z.B. Nitrozellulose, besteht, zu beseitigen, habe ich bei diesem Versuche eine Methode angewandt, nach der man die Veränderung des spezifischen Gewichtes feststellt, und dadurch indirekt die Diffusionsgeschwindigkeit mißt. Es gibt eine Methode, wonach man einen hohlen Zylinder in die Lösung eintaucht, der an einem Ende der Waage hängt und indem man das Gewicht des anderen Endes verändert, damit die Waage das Gleichgewicht erhält, mißt man die spezifischen Gewichte der Lösung, die sich je nach dem Zustande der Diffusion ändert. Diese Methode scheint aber bei diesem Versuche durchaus nicht in Gebrauch zu kommen, weil erstens der obere Teil des Gefäßes offenbleibt, zweitens das Volum des Zylinders verhältnismäßig groß sein muß und drittens die Veränderung der spezifischen Gewichte der kolloidalen Substanz wie Nitrozellulose gering ist,

wenn auch ihre Konzentration steigt. Dabei habe ich versucht, für diese Messung eine empfindliche Feder-waage zu benutzen, aber ich mußte diese Methode erfolglos aufgeben, da ich damit nicht leicht den gewünschten Zweck erreichen konnte.

Die nötigen Formeln, wonach man die Diffusionskonstante aus dem Ergebnis der Messung der Veränderung von spezifischen Gewichten in der Lösung berechnet, konnte ich nicht finden, wenn ich nur die Unterschiede der spezifischen Gewichte für gegebene Zeit nur an einer bestimmten Stelle maß, ohne eine andere Bedingung hinzuzufügen. Die Formel der Messung der Diffusionskonstante, die ich für meinen Versuch benutzte, sind die Drei folgenden :

$$\left. \begin{aligned} u - c_2 &= \frac{c_1 - c_2}{2} \left\{ 1 - 4 \left(\frac{x}{2D^2 \sqrt{t}} \right) \right\} & x > 0 \dots a \\ u - c_2 &= \frac{c_1 - c_2}{2} \left\{ 1 + 4 \left(\frac{x}{2D^2 \sqrt{t}} \right) \right\} & x < 0 \dots b \\ u &= \frac{c}{2} \left\{ 1 - 4 \frac{x}{2D^2 \sqrt{t}} \right\} & c_2 = 0 \dots c \end{aligned} \right\} \dots (1)$$

Das ist die Formel zwischen gelöster bzw. zu lösender Substanz und Diffusionskonstante D , wenn sich eine Lösung mit einer Konzentration c_1 unter einer Lösung mit einer Konzentration c_2 befindet und sie nach einer bestimmten Zeit t in eine Höhe x eine Konzentration u erhält.

$$u = \frac{1}{2} \left\{ 1 - 4 \left(\frac{x}{2D^2 \sqrt{t}} \right) \right\} \dots \dots \dots (2)$$

Das ist die Formel von dem Fall, wo man zuerst die zu lösende Substanz auf den Boden des Gefäßes hineinlegt und das Lösungsmittel in hoher Schicht übergießt. Dann hat die Substanz nach der Zeit t in das Lösungsmittel diffundiert und die Lösung in der vom Boden gemessenen Höhe x eine Konzentration u erreicht, und zwar muß u im x ihre maximale Höhe haben und das Niveau muß nach einer Zeit $t+a$ nach dem Boden des Gefäßes zu hinunterzusinken anfangen. Daher muß man in der Kurve des Maximum suchen, wenn man diese Formel benutzen will. Aber ein Maximum in die Rechnung zu ziehen bringt bei einer solchen Messung sehr leicht einen Fehler. Wie man in den Tafeln sieht, bewegt sich u kaum in der Nähe ihre Maximalwerte, während der Wert des t eine sehr große Distanz hat. Es ergeben sich also im Versuche ungenaue Zahlen. Im Diagramm zeigt sich im Maximum der Kurve vielmehr eine gerade Linie als ein Punkt der Tangente. (vgl. Riemann-Webet "Differentialgleichungen der Physik" Bd. II)

Da es bei den Substanzen wie z.B. Nitrozellulose, die nur langsam diffundieren, vorteilhaft ist, die Konzentration der oberen Schicht, die diffundiert wird gering zu halten, ist es bequemer, den Versuch so zu arrangieren, daß von den ersten Formeln die dritte benutzt werden kann.

Wenn die Probalitätsfunktion in die Formel hineinkommt, beschränkt es die Anwendungsmöglichkeit der Formel und verursacht manchmal auch den Fehler. Deshalb habe ich eine dritte neue Formel entwickelt, um eine Methode zu haben, wonach man auf ganz sichere Weise den Versuch möglichst einfach ausführt und für die Rechnung die genauen Zahlenwerte erhalten kann.

$$\log \frac{c_1}{c_2} = -\frac{1}{4Dt}(x_1^2 - x_2^2) \dots\dots\dots (3)$$

Bei dieser Formel braucht man am Anfang des Versuches nicht die Konzentration der Lösung und dergl. gemessen zu haben. Die Versuchsmethode ist folgende: Man setzt zuerst eine hohe Schicht des Lösungsmittels auf die zu lösende Substanz. Mißt man nach einer Zeit t dessen Konzentration c_1 und c_2 in zwei Stellen der Lösung, deren Höhe je x_1 und x_2 sind, so erhält man zwischen Diffusionskonstante D und c_1 , c_2 , x_1 , x_2 und t folgende Formeln:

$$-\frac{dq}{\partial x} dx dt = \frac{\partial c}{\partial t} dt dx \dots\dots\dots (4)$$

$$-q \propto \frac{\partial c}{\partial x} \dots\dots\dots (5)$$

$$-q = D \frac{\partial c}{\partial x} \dots\dots\dots (6)$$

Setzt man q ins (4) $D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \dots\dots\dots (7)$

Bestimmt man nun $c = T \cos \alpha x$, dabei α als Konstante, als Funktion des t , so befriedigt es zugleich (7) und den Grenzzustand auf dem Boden; denn auf dem Boden, wo $x = 0$ ist, besteht keine Diffusion nach unten, und daher $q = 0$, daher $\frac{\partial c}{\partial x} = 0$, und befriedigt $c = T \cos \alpha x$, falls $x = 0$ ist $\frac{\partial c}{\partial x} = 0$.

Setzt man jetzt $c = T \cos \alpha x$ in (7) und sucht man den Wert des T :

$$-D\alpha^2 T = \frac{\partial T}{\partial t}, \quad T = A e^{-D\alpha^2 t},$$

$$c = Ae^{-D\alpha^2 t} \cos \alpha x, \quad A = \text{Integral konstant.}$$

Bei der Ableitung dieser Formel gelangt man zu folgender Fourierscher Formel:

$$f(x) = \frac{2}{\pi} \int_0^\infty d\alpha \int_0^\infty f(\lambda) \cos \alpha x \cos \alpha \lambda d\lambda$$

Suche ich für die nötige Formel des c was den Initialzustand und den obengenannten Grenzzustand befriedigt, und falls dabei der Initialzustand in $c = f(x) [t = 0]$ gegeben würde, so ist folgendes die Formel von c :

$$c = \frac{2}{\pi} \int_0^\infty d\alpha \int_0^\infty f(\lambda) e^{-D\alpha^2 t} \cos \alpha x \cos \alpha \lambda d\lambda \dots\dots\dots (8)$$

Man kann nun diese Formel folgendermaßen prüfen: Setzt man sie in (7) ein, so wird (7) befriedigt, ferner wenn man, nachdem man (8) und x differenziert und $x = 0$ setzt, so wird $\frac{\partial c}{\partial x} = 0$, und die Formel befriedigt den Grenzzustand. Ausserdem ergibt sich, wenn man in (8) $t = 0$ setzt, aus der Fourierschen Formel $c = f(x)$. Nun beginne ich diese Integralrechnung zuerst mit der des:

$$\int_0^\infty e^{-D\alpha^2 t} \cos \alpha x \alpha d\alpha = \frac{1}{2} \int_0^\infty e^{-D\alpha^2 t} \{ \cos \alpha(x+\lambda) + \cos \alpha(x-\lambda) \} d\alpha \dots (9)$$

Der Wert dieser Gleichung wird aus der Formel

$$\int_0^\infty e^{-a^2 x^2} \cos bx dx = \frac{\sqrt{\pi}}{2a} e^{-\frac{b^2}{4a^2}}$$

erhalten, nämlich setzt man $x = \alpha$, $a^2 = Dt$, $b = x \pm \lambda$, so ergibt sich

$$(9) = \frac{\sqrt{\pi}}{4\sqrt{Dt}} \left(e^{-\frac{(x+\lambda)^2}{4Dt}} + e^{-\frac{(x-\lambda)^2}{4Dt}} \right).$$

Setzt man dies ins (8) ein, so wird

$$c = \frac{1}{2\sqrt{\pi Dt}} \int_0^\infty f(\lambda) \left(e^{-\frac{(x+\lambda)^2}{4Dt}} + e^{-\frac{(x-\lambda)^2}{4Dt}} \right) d\lambda$$

Nimmt man nun für den Initialzustand $c = f(x) [t = 0]$ in folgender Weise, nämlich, wenn $t = 0$ ist, so ist $c = 0$ innerhalb einer dünnen Bodenschicht, wo $0 < x < h$ ist, und $c = 0$ in der darüberliegenden Schicht, wo

$h < x < \infty$ ist. Wegen Einfachheit der Rechnung habe ich den limitierenden Fall $h \rightarrow 0$ nur annähernd festgestellt:

$$c = \frac{1}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \lim_{h \rightarrow 0} \int_0^h f(\lambda) d\lambda$$

Diese, $\lim_{h \rightarrow 0} \int_0^h f(\lambda) d\lambda$ ist integriertes Ergebnis der gesamten innerhalb einer Zeit $t = 0$ in die dünne Bodenschicht, diffundierten Substanz; also es ist nicht anders, als die zu Anfang zugegebene Menge der Substanz, die von der ersten Quelle her stammt. Setzt man dies als M

$$M = \lim_{h \rightarrow 0} \int_0^h f(\lambda) d\lambda$$

Daraus:

$$c = \frac{M}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}, \quad \log_e \frac{\sqrt{\pi Dt}}{M} + \log_e c_1 = -\frac{x_1^2}{4Dt}$$

$$\log_e \frac{\sqrt{\pi Dt}}{M} + \log_e c_2 = -\frac{x_2^2}{4Dt}$$

$$\therefore \log_e \frac{c_1}{c_2} = -\frac{1}{4Dt} (x_1^2 - x_2^2)$$

Um die dritte Formel in dem Versuche unterbringen zu können, habe ich folgende Einrichtung angeschafft; ich konstruierte zunächst einen graduierten Glaszylinder mit dem Deckel, dessen Höhe circa 30 cm. beträgt. In diesen Zylinder habe ich die zu lösende Substanz bzw. eine dünne Schicht der stark konzentrierten Lösung zugesetzt, nachdem sie von den Luftblasen befreit wurde. Darauf goß ich ganz langsam das Lösungsmittel etwa 30 cm. hoch. Der Zylinder wird nun zugedeckt und in einen Thermostat gebracht, dessen Temperatur konstant ist.

Ins Lösungsmittel diffundiert nun die Substanz und nach einer bestimmten Zeit steigt allmählich die Konzentration. Um sie zu messen, stellte ich kleine Aräometer her. Ihr spezifisches Gewicht reguliert man nach Belieben, entweder durch Abfeilen oder Ankleben von etwas Glasur. Man bringt sie in den Zylinder und liest ihre Höhe an der am Zylinder angegebenen Skala ab.

Der Vorteil dieser Einrichtung besteht darin, daß man mehr als zwei Aräometer in einen Zylinder bringen und dauernd den Diffusionszustand der Lösung messen kann. Ausserdem kann man die Aräometer beliebig

Nr. des Versuches	Name des Objektes	Konstante aus der Messung	In der Literatur angegebene Konstante	Dauer in Tagen	c_1	c_2	x_1	x_2	Nr. der zu der Rechnung angewandten Formel
1	KJ	1.47	1.1~1.46 ~1.55	55	0.021	0.028	10.75	14.45	(3)
2	„	1.53	„	46	0.046	0.051	15	14	(3)
3	„	1.41	„	50	0.021	0.028	9.8	13.3	(3)
4	„	1.14	„	24	$u=0.563$, $u=0.042\text{mol.}$	$c=13.4$, $c=1.00\text{ mol.}$	$x=12.9\text{ cm.}$		(1)
5	BaCl ₂	0.925	0.66	21	0.006	0.024	12	6	(3)
6	„	1.54	„	78	0.006	0.021	18	12	(3)
7	„	1.38	„	15	0.006	0.016	15	12	(3)
8	„	1.52	„	27	0.006	0.016	22.6	16	(3)
9	„	1.70	„	90	0.026	0.031	15.6	11.2	(3)
10	„	1.37	„	43	0.016	0.021	17	15	(3)
11	„	1.17	„	15	0.006	0.016	13	10	(3)
12	„	1.03	„	48	0.016	0.021	19	17	(3)
13	CaCl ₂	0.690	0.7	49	0.016	0.021	21	19.5	(3)
14	„	0.901	„	54	0.006	0.021	25	22.0	(3)
15	Glyzerin	0.705	0.30~0.79	85	0.006	0.016	17.4	77	(3)
16	„	0.732	„	155	0.011	0.016	14.9	12.1	(3)
17	„	0.740	„	131	0.011	0.016	13.3	106	(3)
18	Alkohol + Wasser	0.603		131	0.088	0.108	9.4	5.0	(3)
19	Azeton + Wasser	0.720		99	0.066	0.070	14.7	11.3	(3)
20	„	0.744			$u=250/18$,	$x=4\text{ cm.}$	$c=999/18$	$t=60$	(1)
21	Naphtolgelb	0.439 cm./Tg. (0.508 cm. /sek. $\times 10^{-5}$)	0.47/sek.	35	0.001	0.006	12	11	(3)
22	„	0.382 cm./Tg. (0.443 cm. /sek. $\times 10^{-5}$)			$u=0.006$,	$c=3/40$,	$x=6.8$,	$t=174\text{ Tg.}$	(1)
23	„	0.441 cm./Tg. (0.511 cm. /sek. $\times 10^{-5}$)			$u=0.006$,	$c=3/40$,	$x=9$,	$t=170\text{ Tg.}$	(1)

Nr. der Versuches	Name des Objektes	Konstante aus der Messung	In der Literatur angegebene Konstante	Dauer in Tagen	c_1	c_2	x_1	x_2	Nr. der zu der Rechnung angewandten Formel
24	Eosin	0.0253 cm./Tg. (0.0293 cm./sek. $\times 10^{-5}$)	0.033 cm./sek.	61	0.001	0.006	23.2	23.0	(3)
25	Eosin	0.0355 cm./Tg. (0.0411 cm./sek. $\times 10^{-5}$)		62	0.001	0.006	19.8	19.6	(3)
26	Milch Zucker		(0.27, 0.37)						
27	„	0.281			$u=0.026,$	$c=12/75,$	$x=1.05,$	$t=91$ Tg.	(1)
28	„	0.290			$u=0.26,$	$c=12/75,$	$x=0.6,$	$t=26$	(1)
29	„	0.296		0.99	0.006	0.016	9.2	5.9	(3)
30	„	0.230			$u=0.026,$	$x=1.1$ cm.,	$t=122$		(2)
31	Traubenzucker	0.545	0.56	27	0.004	0.013	9.3	4.7	(3)
32	Mannit	0.194	(0.4—0.5)	30	0.004	0.007	8.1	7.2	
33	„	0.197		73	0.001	0.006	14.7	10.7	
34	Oxalsäure	1.07	(0.61—0.71)	131	0.004	0.008	22.2	10.5	(3)
35	„	0.90			$u=6/45,$	$c=0.006,$	$x=17.4$ cm.	$t=152$	(1)
36	„	0.872			$u=8/45,$	$x=47$ cm.,	$t=138$		(2)
37	Weinsäure	0.381	(.34—.43)	31	0.004	0.009	11.4	9.5	(3)
38	„	0.451		122	0.006	0.008	49.7	42.1	(3)
39	„	0.376		38	0.006	0.016	37.7	20.0	(3)
40	Urea	0.978	(0.97)	48	0.006	0.016	15.7	7.4	(3)
41	„	1.103		15	0.006	0.016	10.6	6.8	(3)
42	„	0.926		18	0.006	0.016	10.2	6.5	(3)
43	Pepsin	0.129 (150 cm./sek $\times 10^{-5}$)	(0.073 cm./sek.)	62	0.004	0.006	11.1	10.5	(3)

Name des Objektes	Zahl des Kohlenstoffes	Zahl der Elemente	Konstante aus der Messung	Dauer in Tagen	c_1	c_2	x_1	x_2	Nr. der zu der Rechnung angewandten Formel
Kalium Propionat	3	11	0.608						
„			0.230	31	0.004	0.006	8.6	7.9	(3)
Kalium Lactat	4	14	0.205	61	0.004	0.006	9.8	8.7	(3)
Kalium Valeriat	5	17	0.625	10	0.006	0.011	9.3	4.7	(3)
„			0.625	10	0.006	0.011	9.1	4.8	(3)
„			0.632	36	$u = 0.004$, Max. Höhe = 9				(2)
Kalium Palmitat	16	50	0.117	16	0.006	0.011	3.3	3.0	(3)
Kalium Stearat	18	56							

Name des Objektes	Konstanten	Data aus Messungen	Formel	Bemerkung
Zellulose Acetat	0.572	$t = 91, x = 1.25, u = 0.012, c = 1.554/50$	(1)	
„	0.619	$t = 40, x = 0.3, u = 0.002, c = 0.88/50$	(1)	
„	0.639	$t = 81, x = 2.5, u = 0.010, c = 1.554/50$	(1)	
„	0.646	$t = 104, x = 2.9, u = 0.010, c = 1.554/50$	(1)	
Nitrozellulosen mit höheren Stickstoffgehalt (11)	0.546	$t = 91, x = 2.15, u = 0.007, c = 1.158/50$	(1)	
„ (11)	0.596	$t = 90, x = 2.5, u = 0.007, c = 1.158/50$	(1)	
„ (2)	0.633	$t = 110, x = 0.85, u = 0.007, c = 0.776/50$	(1)	
„ (6)	0.651	$t = 31, x = 3.8, u = 0.003, c = 0.2322$		
Nitrozellulosen mit niedrigen Stickstoffgehalt (1)	0.701	$t = 91, x = 0.75, u = 0.007, c = 0.776/50$		
„ (1)	0.695	$t = 81, x = 4.7, u = 0.006, c = 1.158/50$		
„ aus Pulp	0.0255	$t = 58, c_1 = 0.004, c_2 = 0.008, x_1 = 4.4, x_2 = 3.9$		
„ aus Pulp	0.0253	$t = 60, c_1 = 0.002, c_2 = 0.008, x_1 = 4.7, x_2 = 3.7$		Film
„	0.0528	$t = 110, c_1 = 0.006, c_2 = 0.011, x_1 = 6.6, x_2 = 5.4$		
Gelatinierungsmittel	0.0826	$t = 32, c_1 = 0.005, c_2 = 0.010, x_1 = 6.4, x_2 = 5.8$		Gemisch
Gewehrpulver	0.116	$t = 30, c_1 = 0.005, c_2 = 0.007, x_1 = 6.65, x_2 = 6.3$		„

Name des Objektes	Beleucht- ung	Kon- stanten	Resultat von Messungen						For- mel
Nitrozellu- losen mit höheren Stickstoff- gehalt	keine	0.546	$t = 91$	$x = 2.15$	$u = 0.006$	$c = 1.158/50$		(1)	
„	5 Stunde	?							
„	10 Stunde	0.589	$t = 82$	$x = 3.5$	$u = 0.005$	$c = 1.158/50$		(1)	
„	keine Erhitzt 100°C. 24 Stunde	0.837	$t = 117$	$x = 5$	$u = 0.004$	$c = 0.753/50$		(1)	
Nitrozellu- losen mit niedrigen Stickstoff- gehalt	keine	0.550	$t = 91$	$x = 1.9$	$u = 0.005$	$c = 0.776/50$		(1)	
„	5 Stunde	0.563	$t = 111$	$x = 2.2$	$u = 0.005$	$c = 0.776/50$		(1)	
„	10 Stunde	0.633	$t = 96$	$x = 0.7$	$u = 0.007$	$c = 0.776/50$		(1)	
„	„	0.650	$t = 110$	$x = 0.8$	$u = 0.007$	$c = 0.776/50$		(1)	
Nitrozellulose	keine	0.437	$t = 70$	$x = 4.5$	$u = 0.006$	$c = 1.554/50$		(1)	
„	5 Stunde	0.464	$t = 67$	$x = 2.4$	$u = 0.009$	$c = 1.554/50$		(1)	
„	10 Stunde	0.487	$t = 81$	$x = 2.3$	$u = 0.007$	$c = 1.554/50$		(1)	
Nitrozellu- losen mit niedrigen Stickstoff- gehalt (Film)	keine	0.0528	$t = 110$	$c_1 = 0.006$	$c_2 = 0.011$	$x_1 = 5.2$	$x_2 = 4.0$	(3)	
„	gebeleuchtet	0.098	$t = 109$	$c_1 = 0.005$	$c_2 = 0.007$	$x_1 = 5.0$	$x_2 = 3.6$	(3)	
Gelatinier- ungsmittel	keine unerhitzt	0.083	$t = 32$	$c_1 = 0.005$	$c_2 = 0.010$	$x_1 = 6.4$	$x_2 = 5.8$	(3)	
„	Erhitzt 135°C. 6 Stunde	0.144	$t = 30$	$c_1 = 0.005$	$c_2 = 0.010$	$x_1 = 7.05$	$x_2 = 6.2$	(3)	
Gewehr- pulver	unerhitzt	0.116	$t = 30$	$c_1 = 0.005$	$c_2 = 0.007$	$x_1 = 6.65$	$x_2 = 6.3$	(1)	
„	Erhitzt 135°C. 6 Stunde	0.193	$t = 30$	$c_1 = 0.005$	$c_2 = 0.01$	$x_1 = 7.1$	$x_2 = 6.3$	(3)	

klein machen, sodaß man sie schließlich nur noch als Punkt betrachten kann. Man vermeidet ferner nach dieser Methode die Zerstörung des Diffusionszustandes oder der Temperaturschwankung der oberen Schicht. Nach den obengenannten anderen Methoden lassen sich diese Fehler nicht vermeiden. Mit einer einzigen Einrichtung läßt sich die von Zeit zu Zeit sich verändernde Konzentration der Lösung nicht messen.

Messungen der Diffusionskonstante.

Ich habe einige Substanzen, deren Diffusionskonstanten bereits in der Literatur angegeben sind, ausgewählt, und habe selbst ihre Diffusion gemessen und die Konstante daraus berechnet. Folgende Tabellen zeigen die Ergebnisse der Messungen. Als Einheiten werden Tage und cm. angegeben.

Aus den oben angegebenen Tabellen ersieht man, daß die Diffusionskonstante, die ich aus meinen Versuche erhalten habe, mit der der Literatur bei relativ vielen Substanzen fast übereinstimmt. Daher kann diese Arbeitsmethode auch als eine zu Bestimmung der Diffusionskonstante berücksichtigt werden. Versuche 1-4, Messungen an Kaliumjodid, sind besonders wertbestimmende Beispiele für die Genauigkeit meines Versuches. Obwohl die Versuche jedesmal einzeln und in verschiedenen Gefäßen durchgeführt wurden, stimmen die aus diesen Versuchen erhaltenen Konstanten fast alle überein. Dies beweist, daß die von mir ausgearbeitete Methode in allen Fällen angewandt werden kann. Ausserdem stammen alle angegebenen Werte nicht von einer einmaligen Messung, sondern es sind nur solche berücksichtigt, die im Vergleich zu den vor bzw. nach 1-2 Wochen ausgeführten Messungsergebnissen fast übereinstimmen. Nur bei Mannit habe ich im Vergleich zur Angabe in der Literatur andere Werte erhalten. Da aber die Werte, die ich von verschiedenen Proben erhielt, immer dieselben waren, so habe ich sie vorläufig auch mit eingeführt.

Die Diffusionskonstante der Seife konnte ich in der Literatur nicht finden. Aber durch Vermutung, daß zwischen Diffusionskonstante und Zahlen der Atome eine Abhängigkeit bestehen könne, habe ich aus verschiedenen Fettsäuren Kalisalze hergestellt und versucht, ihre Diffusionskonstante zu messen. Es schienen mir bei Valeriansäure alle beiden Versuche (in 2 verschiedenen Gefäßen) glatt gelungen zu sein, aber bei allen anderen musste ich die Versuche aufgeben, weil ich wegen des Mangels an Versuchsdauer oder wegen zu geringer Veränderung der spezifischen Gewichte der Objekte keine befriedigenden Resultate erhalten konnte. Es ist auch möglich, daß diese negativen Ergebnisse für die

Seifenarten normal sind, und die Versuche mit Valeriansäuren-Kali aus einem anderen zufälligen Grunde wie z. B. Verunreinigung des Materials so glatt verlaufen sind.

Die Messung der Diffusionskonstante ist bei den löslichen Substanzen leicht, falls die Lösung aber kolloidal ist wie z. B. bei Nitrozellulose, ist der Versuch mit verschiedenen Schwierigkeiten verbunden und man muß ihn daher mit größter Sorgfalt durchführen.

Besonders die Luftblasen, selbst wenn sie sehr gering sind, geben eine der wichtigsten Fehlerquellen ab und sie müssen daher streng vermieden werden. Aus diesem Grunde habe ich ein Versuchsmaterial wie z. B. Nitrozellulose in eine geringe Menge von Lösungsmittel gebracht und genügend lange Zeit auf dem Gefäßboden stehen lassen. Nachdem nun die Luftblasen usw. verschwunden sind, habe ich darüber das Lösungsmittel in genügend hoher Schicht zugesetzt. Die Vorbereitung des Versuchsmaterials kann noch in mancher Hinsicht verbessert werden. Ausserdem benutzte ich zuerst als Versuchsgefäß einen gewöhnlichen Messzylinder. Da nun ein Messzylinder nur zur Volumenbestimmung dient und seine Graduierung in bezug auf die Höhe oft ungleichmäßig ist, mußte ich sie vorher korrigieren, um diese Fehlerquelle zu vermeiden. Trotz dieser Sorgfalt stieß ich oft auf Ungenauigkeiten und ich nahm später einen gleichweiten graduierten Zylinder und führte nun die Versuche nebeneinander in beiden Gefäßen aus.

Die wichtigsten Bedingungen bei diesem Versuche sind das spezifische Gewicht des Aräometers genau festzustellen und die Höhe genau abzulesen. Infolgedessen ist es sicherer, wenn man, um den Einfluß der dem Aräometer anhaftenden Luftblase auszuschalten, dieses möglichst nach langer Zeit ins Gefäß zu setzen und gleich die Messung zu machen. Der Grund, daß ich die Formel 1 bzw. 2 oder 3 zur Rechnung anwandte, waren nur Bequemlichkeiten für die Rechnungen, die je durch die Resultate des Versuches bedingt sind. Wenn man jetzt den Aggregatzustand der Moleküle aus der Diffusionskonstante der verschiedenen Nitrozellulosen, die anscheinend durch Bestrahlung bzw. durch Erhitzung ihre Diffusionskonstanten verändert sind, herauszurechnen versucht, so wird es folgendermaßen durchgeführt.

Die hierzu nötige Formel ist:

$$DM^{1-n} = k$$

$$\frac{M_1}{M_2} = \left(\frac{D_2}{D_1} \right)^2, \quad n = 1.5$$

Dabei sind: D_1 und D_2 je Diffusionskonstanten und M_1 , M_2 je Molekulargewichte.

Dispersionsgrad des Nitrozellulosen-Moleküls.

Versuchsobjekte	D_2	D_1	$\frac{M_1}{M_2}$	Bemerkung
höhere Nitrozellulose	0.589	0.546	1.17	10 Std. bestrahlt
„ „	0.837	„	2.35	24 „ bei 100°C
niedrige „	0.563	0.550	1.05	5 „ bestrahlt
„ „	0.633	„	1.32	10 „
„ „	0.650	„	1.39	10 „

Bemerkung: Die Baumwolle, welche ich hierbei anwandte, war nicht diejenige, deren $D = 0.54$ zeigte. Der Grund dafür, daß ich hier das bestrahlte und unbestrahlte Dunloppulver und den bestrahlten und unbestrahlten gelatinierten Sprengstoff verglich, obwohl sie unrein und in bezug auf Messung der Konstante von geringer Bedeutung sind, liegt darin, daß ich dadurch hoffte, sie für die Prüfung des Grades von der Veränderung der Waren mehr oder weniger benutzen zu können. Die Versuchsobjekte, die in dünnen Blättchen erhältlich waren, habe ich ohne sie vorher mit dem Lösungsmittel zu mischen, auf den Boden gelegt. Deshalb habe ich von solchen Objekten kleinere Diffusionskonstanten erhalten. Ferner nehme ich an, daß der Versuch mit nitriertem Pulp einen zu kleinen Wert ergab, weil er vor den Sommerferien ausgeführt wurde und die Mischung (vielleicht Diffusion) nicht vollständig beendet war. Diese Konstanten können vielleicht zur Berechnung der Grösse von Zellulosenmolekülen oder der Aggregationszahl der Moleküle angewandt werden.⁽¹⁾

Aus der oben zitierten Rechnung ersieht man, daß der Dispersionsgrad des bei 100°C. erhitzten Nitrozellulose mehr als doppelt so groß ist wie der der normalen Baumwolle. Daher liegt die Vermutung nahe, daß der Aggregationsgrad der Moleküle verkleinert ist. Um dieses genauer festzustellen, habe ich mit einem Strukturviscosimeter nach Prof. Wolfgang Ostwald, die Strukturbildung der unerhitzten und in derselben Kapillare ca. 100 Stunden lang erhitzten Mischung von Nitrozellulose, normaler Baumwolle und von Aceton vergleichen. Die erhitzten Proben zeigten im Vergleich zu anderen eine geringe Steigerung der struktiven Gebiete. Dies läßt sich vielleicht dadurch erklären, daß bei einem Kolloide das Teilchen durch Erhitzen verkleinert wird. Aber die zu diesem Versuche benutzten Baumwollarten waren einige Jahre schon deponiert, sodaß der Verdacht besteht, daß sie inzwischen degeneriert sind. Benutzt man aber zu diesem Versuche frisches Material, so würden evtl. Unterschiede zwischen erhitzten und unerhitzten Materialien größer sein.

Herrn Prof. J. Sameshima und Herrn Dr. S. Sakai danke ich für seinen Hilfen.

(1) Vgl. Herjog, J. Phys. Chem., 3 (1926).

OBSERVATIONS ON THE ABSORPTION SPECTRA
OF THE RARE EARTHS. II.

By Yasumitsu UZUMASA.

Received December 14th, 1931. Published March 28th, 1932.

The absorption spectra give invaluable clews in the rapid estimation of the coloured rare earth salts since we have no other satisfactory chemical means of detecting the elements of this family. The bands, however, are often changed both in positions and in intensities by change in the conditions under which observations are made, e.g., by changing concentration or by adding other substances. The spectra should therefore be used with the utmost caution only for the qualitative purpose. In the first paper of this series⁽¹⁾ the writer has pointed out that the bands of neodymium nitrate and also of praseodymium nitrate are shifted toward the longer wave-lengths when they are dissolved in some organic solvents, the shifts increasing as the dielectric constant of the liquid decreases. The present work was undertaken with the object of obtaining further knowledge as to the shifts of the bands of neodymium salts.

Experimental.

Material and Apparatus. The neodymium oxide used was the same one as used in the previous work. It was Prof. Rolla's preparation and of 99.99% purity. Each spectrum was photographed by a constant deviation spectrograph constructed in the workshop of the Institute of Physical and Chemical Research, Tokyo. As the source of illumination a tungsten lamp was used. The solutions were held in a glass tube, 5 or 10 cm. in length, provided with glass end plates.

Absorption of $\text{Nd}(\text{NO}_3)_3$ and NdCl_3 in Various Solvents. It has long been known that in some cases different salts of the same element yield bands of different wave-lengths when dissolved in the same solvent. The absorption of the aqueous solution of neodymium nitrate, for example, is a little different from that of neodymium chloride at a certain higher concentration⁽²⁾. This is supposedly due to the fact that the negative field produced by the nitrate ion differs in intensity from that produced by the chloride ion so that the electron shells of the neodymium ion are deformed in a more or less different manner in each case.

(1) This Bulletin, **6** (1931), 147.

(2) *Proc. Camb. Phil. Soc.*, **12**, 206.

As reported in the previous paper the oppositely charged ions are brought closer to one another with considerably marked changes of the bands when the salt is dissolved in a liquid of low dielectric constant. It seems now probable that nitrate and chloride of neodymium might produce different spectra, if dissolved in such a liquid, even at such a low concentration that they might produce similar spectra if dissolved in water. An attempt was therefore made to compare the spectra of neodymium chloride and nitrate dissolved in alcohol and in other organic solvents.

In each case 0.1 gr. of neodymium oxide was dissolved in nitric or hydrochloric acid and excess acid then removed. As the chloride is less soluble in those organic solvents used than the nitrate, each salt was first dissolved in 6 c.c. of water and the volume of the solution was made up to 50 c.c. with the individual solvent, i. e., ethyl alcohol etc. The spectra of the chloride and the nitrate in the same solvent were then compared.

Fig. 1 shows the spectra of the salts dissolved in water. A represents the absorption of the chloride and B that of the nitrate. At this concentration (0.0119 mol.) both are practically identical. Fig. 2 shows the spectra of glycerol solutions. The two are with difficulty distinguishable. Of the methyl alcohol solutions, however, the bands of the nitrate are shifted more markedly than those of the chloride, in spite of the concentration with respect to Nd^{+++} being exactly the same as before. In the ethyl alcohol solutions the difference is as plain as in the methyl alcohol solutions. These two cases are shown in Figs. 3 and 4. The difference becomes more conclusively apparent when the acetone solutions are examined. As shown in Fig. 5, the band in the $5750 \text{ \AA}$ region of the nitrate is unmistakably spread out and shifted nearly $45 \text{ \AA}$ toward the red as compared with the same band of the chloride. In the nitrate solution the band at $5220 \text{ \AA}$ and that at $4275 \text{ \AA}$ are both shifted more redward and the two bands in the $5100 \text{ \AA}$ region merge into one another. Comparison was also made with the concentrated aqueous solutions (0.476 mol.) in which case the nitrate likewise develops greater displacements than the chloride. (Fig. 6)

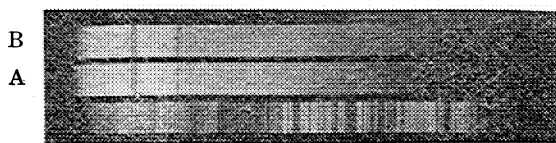


Fig. 1.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in water. (0.0119 mol., 10 cm.)

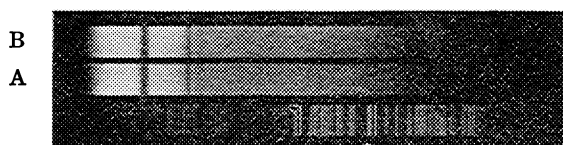


Fig. 2.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in glycerol. (0.0119 mol., 10 cm.)



Fig. 3.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in methyl alcohol. (0.0119 mol., 10 cm.)



Fig. 4.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in ethyl alcohol. (0.0119 mol., 10 cm.)



Fig. 5.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in acetone. (0.0119 mol., 10 cm.)

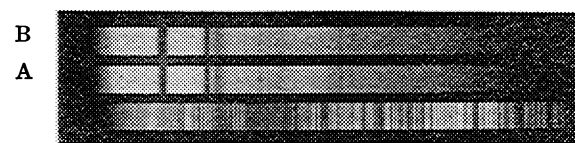


Fig. 6.—The absorption spectra of neodymium chloride (A) and nitrate (B) dissolved in water. (0.476 mol., 1 cm.)

Changes of the Bands of $\text{Nd}(\text{NO}_3)_3$ produced by Ether, Benzene etc. It was next desired to examine possible changes of the bands to be observed when neodymium nitrate was dissolved in a liquid having a dielectric constant lower than those used in the previous experiments. For this purpose ether, benzene, carbon tetrachloride and chloroform were used. Neodymium nitrate, however, is practically insoluble in these solvents when the liquids are used in the pure state. Each solvent was therefore mixed with ethyl alcohol to a certain ratio and then in the mixture the salt was dissolved. In Fig. 7, A and C represent the spectra of $\text{Nd}(\text{NO}_3)_3$ in pure ethyl alcohol while B that in the mixture ethyl alcohol + ether (1 : 4 by volume). In the latter solution, the band in the 5750 Å region is intensified and shifted slightly toward the red, the same band in the former solution being taken as standard. The band at 5220 Å is also shifted in some measure toward the red in the mixed solvent.



Fig. 7.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+ether (B). (0.0119 mol., 5 cm.)

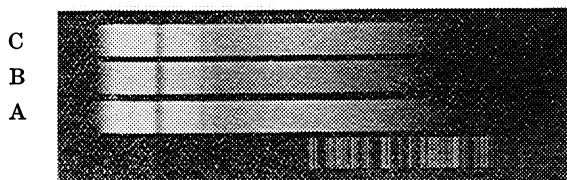


Fig. 8.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+benzene (B). (0.0119 mol., 5 cm.)

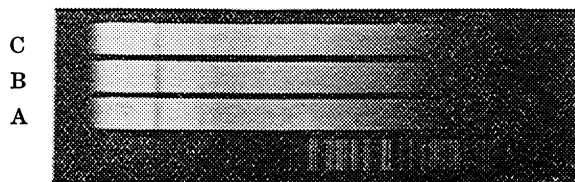


Fig. 9.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+carbon tetrachloride (B). (0.0119 mol., 5 cm.)

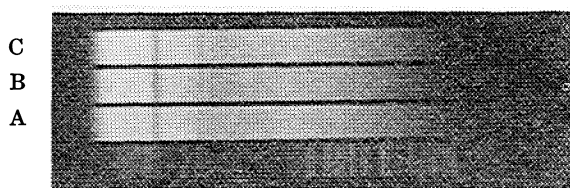


Fig. 10.—The absorption spectra of neodymium nitrate dissolved in ethyl alcohol (A and C) and in ethyl alcohol+chloroform (B).
(0.0119 mol., 5 cm.)

The next examination was made with the ethyl alcohol-benzene solution. It was very interesting to find in the mixed solvent that the displacements of the bands in the 5750 Å region and at 5220 Å are slightly smaller or, in other words, that these two bands were shifted less redward than in the pure alcohol. Similar changes, i.e., the displacements of the bands toward the blue, were observed when the mixture of ethyl alcohol and carbon tetrachloride or ethyl alcohol and chloroform was used instead of pure ethyl alcohol. The concentration of the solutions was always 0.0119 mol. and the observations were carried out through a depth of 5 cm. of the solutions. The results are shown in Figs. 8-10.

Discussion.

Neodymium chloride and nitrate when dissolved in a solvent of low dielectric constant show a marked difference even at rather a low concentration. This is exactly what has been expected and the fact that the difference becomes more apparent with decreasing dielectric constant of solvents indicates well that the shifts are to be produced by the field of the nitrate or other anion. The changes observed with the concentrated aqueous solution confirm this view as well.

The solvation of ions has not been taken into account in the interpretation so far. However, the changes of the bands observed when benzene, carbon tetrachloride or chloroform was mixed with ethyl alcohol in which neodymium nitrate was dissolved seem to be better explained by presuming that the solvent molecules play a part in this phenomenon. D. M. Murray-Rust and others state as to the solvation of ions and its relation to ionic dissociation⁽¹⁾:

" The solvent therefore affects the conductivity of an electrolyte dissolved in it in a variety of ways. First, by the magnitude of its dielectric constant it determines the force of attraction between the ions

(1) *Annual Rep., Chem. Soc.*, **27** (1930), 357.

and the energy needed to separate them. Then, the solvation of the ions appears to exert a decisive influence on the extent to which they form ion pairs or undissociated molecules, and in this respect the power of the solvent molecules to co-ordinate with both ions appears to be even more important than their dipole character. . . .”

It is no doubt true that the neodymium ion is surrounded by molecules of water in which the salt is dissolved. That neodymium nitrate or chloride forms hexahydrate in the solid state suggests some of those water molecules being held in the solution by co-ordinate linkage. In addition to any molecules thus chemically combined, there may be a layer of molecules oriented by their own dipole character and it is difficult to distinguish in which state the solvent molecules exist in the neighbourhood of the neodymium ion. This question shall be put aside awhile as it is not very important to ascertain this in the present discussion. It is by all means possible, however, that the water molecules exert *some* influence over the neodymium ion. Thus in a concentrated solution, a deformation of the electron shells of the neodymium ion is brought about not only by the nitrate ion but also by the water molecules while in a dilute solution this is done mainly by the water molecules.

When dissolved in ethyl alcohol, the nitrate ion will come nearer to the neodymium ion than in the case of water solution. But as is well known this solvent still has the tendency of forming solvate and its molecules have dipole character so that the neodymium ion should never be quite free from the solvent molecules. In other words, the neodymium ion is, in the alcoholic solution, subjected to the combined force of the nitrate ion and the alcohol molecules. Consequently the bands are shifted in great measure toward the red.

What will happen then when the salt is dissolved in a mixture of ethyl alcohol and benzene? Benzene being a normal liquid has no tendency of associating with solute and is actually non-polar. Consequently benzene molecules behave rather indifferently in this case by which is meant that the neodymium ion is left under the influence of the nitrate ion and the alcohol molecules. In this solution the number of alcohol molecules in question should be much smaller so that the bands are shifted as a matter of course less redward. The same interpretation may be made for the changes of the bands observed in the case of alcohol-carbon tetrachloride and alcohol-chloroform mixtures. Ether is known to have abnormal properties though it is a normal liquid in the pure state and it is therefore no wonder that the shifts increase when ether is mixed with alcohol.

In conclusion it is suggested from the present investigation that the displacements of the bands of neodymium salts are produced by solvent molecules as well as by the nitrate or other anion.

Summary.

1. The absorption spectra of chloride and nitrate of neodymium in various organic solvents were compared.
2. The changes of the bands of neodymium nitrate produced by adding a normal liquid to the alcoholic solution were examined.
3. It is suggested that the absorption bands of neodymium salts are shifted by solvent molecules as well as by the anion.

Chemical Department, Faculty of Science,
Hokkaido Imperial University, Sapporo.

**SOME EXPERIMENTS WITH PEROWSKITE ($\text{CaO} \cdot \text{TiO}_2$)
AND TITANITE ($\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$).**

By **Keizô IWASÉ** and **Masaji FUKUSIMA**.

Received December 28th, 1931. Published March 28th, 1932.

Synopsis.

In the experimental study of the equilibrium of the system consisting of calcium silicate, $\text{CaO} \cdot \text{SiO}_2$, and titanium dioxide, TiO_2 , calcium titanate, a compound belonging to the other system has often been found in the crystallized mass of a compound $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$, calcium titanium silicate, and hence thorough investigation of the crystallization of calcium titanate and calcium titanium silicate was carried out before the determination of the equilibrium of the above mentioned system. These two compounds were synthesized from their components and their X-ray patterns were taken by the Debye-Scherrer method, and using these photographs as the standard, the condition has been fully determined in which these two compounds separate out from the melt. Microscopic study with a reflected light has also been applied for the identification of these two compounds. The stabilities of these two compounds were also investigated by several methods. Finally, the melting point of calcium titanium silicate was determined by the cooling curve method in which supercooling of the melt was prevented by seeding.

Introduction.

CaO, SiO₂ and TiO₂ unite in equi-molecular proportions to form the compound CaO · TiO₂ · SiO₂ which is also found in nature as titanite. It is considered unstable in the molten state⁽¹⁾ and another compound named perovskite having the formula CaO · TiO₂ is said to crystallize out from the melt⁽²⁾. On the contrary, in a paper recently published⁽³⁾, no perovskite was observed in the cooled mass of molten titanite. However, in the course of the study of the equilibrium of the system consisting of CaO · SiO₂ and TiO₂ carried out by one of the present authors, perovskite was often observed in the crystallized mass containing titanite. Hence it has been necessary to determine in what condition perovskite does crystallize out from the molten titanite and to decide whether perovskite or titanite is stable in the system consisting of the equi-molecular mixture of CaO, SiO₂ and TiO₂.

Experimental.

I. Preparation of Perovskite and Titanite. Since native perovskite and titanite were not available for the present authors, these specimens were made synthetically from their respective components. Instead of CaO, CaCO₃ was used because the former contains more or less moisture and is not in a suitable form for accurate weighing. CaCO₃ and SiO₂ (quartz sand) used here were Kahlbaum's preparation ("for analytical purpose"). TiO₂ was prepared from TiCl₄ as follows:—Kahlbaum's TiCl₄ was first treated with Na-amalgam, then it was twice distilled, once in vacuo and once in the ordinary way and in this manner the distillate coming off at 134.87°C., 745.1 mm. Hg, was collected.⁽⁴⁾ It was then diluted with distilled water, and then it was precipitated by NH₄OH. The precipitate thus formed was thoroughly washed with hot distilled water, dried and then ignited in a platinum crucible by a platinum wound furnace at 1300°C. for 2 hours. The results of the analysis of TiO₂ thus prepared have proved that its purity is over 99%.

(1) *Perovskite* (CaO · TiO₂). Equi-molecular quantities of CaCO₃ and TiO₂ were thoroughly mixed in an agate mortar by grinding them together. Then the whole of the mixture was carefully transferred to a platinum crucible and was heated to 1500°C. for 4 hours in a platinum wound furnace to let it sinter.⁽⁵⁾ Under microscopical examination this sintered

(1) Doelter, *Handbuch der Mineralchemie*, Bd. III, 1 Teil (1918), 65; W. Eitel, *Physikalische Chemie der Silikate*, (1929), 325.

(2) Ibid; S. Smolensky, *Z. anorg. Chem.*, **73** (1912), 302.

(3) Fukuda, *Journ. Japan. Assoc. Mineralogist etc.* (Sendai), **5** (1931), 35.

(4) Sagawa, to be published in near future.

(5) P. Niggli, *Z. anorg. Chem.*, **98** (1916), 298.

mass was found to contain some new-crystalline product which was supposed to be perowskite. The sintered mass was again ground in an agate mortar in order to confirm the intimate mixing and then was subjected to a second sintering as before. Then by an oxy-hydrogen or an oxy-acetylene flame, the sintered mass was melted. Sometimes, a reduction took place which could be distinguished by the naked eye by the blue color of the fused mass, although care was taken not to reduce the oxides by controlling the amount of oxygen in the fusion. This bluish mass had a structure under the reflected microscope such as is shown in Photo. 1. The round grains seen in the photograph are thought to be perowskite and the dark parts distributed at the boundaries of the round grains, to be a lower oxide of titanium. It was changed to a white coloured substance by heating at a high temperature in the open air. The black spots distributed irregularly in the photograph are the holes formed in the course of polishing the specimen for microscopic purposes. In many cases, by making a careful adjustment of the nature of the flame, the reduction was prevented and homogeneous fused product was obtained, the structure of which is represented in Photo. 2. This homogeneous substance appears reddish brown and experiment by means of a picnometer points to the value 4.028 for its density. In the literature on the subject, the density of perowskite ranges from 4.02 to 4.04 and its colour is pale yellow, reddish brown or grayish black.⁽¹⁾ Therefore the homogeneous crystal above mentioned may safely be concluded to be perowskite. Photo. 3 shows its X-ray spectra taken by the Debye-Scherrer method. According to G. R. Levi and G. Natta,⁽²⁾ the crystal lattice of perowskite was determined as pseudo-cubic.

(2) *Titanite* ($\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$). Equi-molecular quantities of CaCO_3 , SiO_2 and TiO_2 were put into a platinum crucible and were then heated in a platinum furnace and melted. After the melt was thoroughly agitated by a platinum wire, it was then crystallized at about 1380°C . without allowing it to supercool. This was done by throwing a nucleus into the melt at a temperature not lower than 1300°C . (see IV). The crystallized mass appears light green or blue, has a density of 3.497, and is homogeneous as is shown in Photo. 4. In the literature on the subject, the colour of titanite is bluish and its density ranges from 3.4 to 3.56.⁽³⁾ Therefore, this homogeneous crystal may be said to be titanite. Photo. 5 is its X-ray spectra taken as before. According to W. H. Zachariasen⁽⁴⁾, the crystal lattice of titanite is monoclinic holohedral.

(1) J. W. Mellor, *Compreh. Treat. Inorg. Theor. Chem.*, **7** (1927), 53, 54.

(2) *Ibid.*

(3) Doelter, *loc. cit.*

(4) Zachariasen, *Z. Kristallogr.*, **73** (1930), 7.

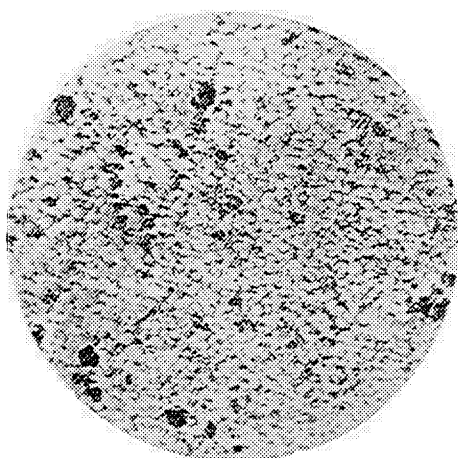


Photo. 1. Perovskite partly reduced. $\times 100$

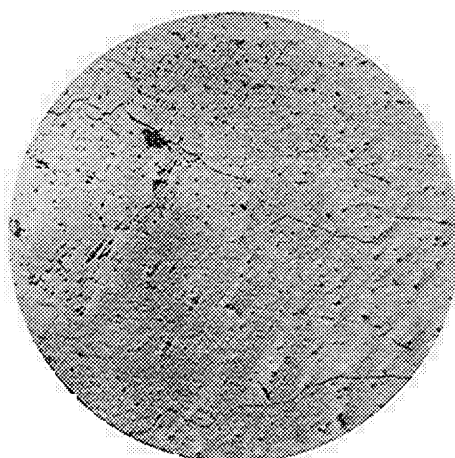


Photo. 2. Perovskite. $\times 100$

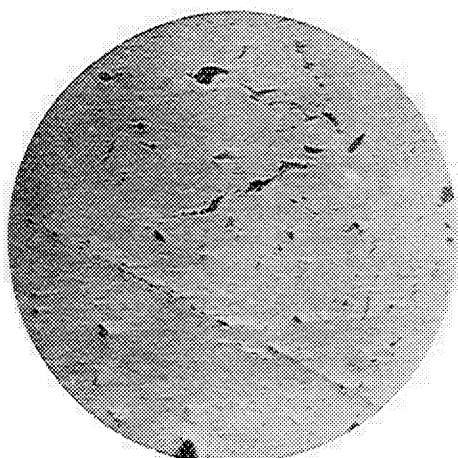


Photo. 4. Titanite. $\times 100$



Photo. 6. Titanite, Perovskite and Silica.
 $\times 100$

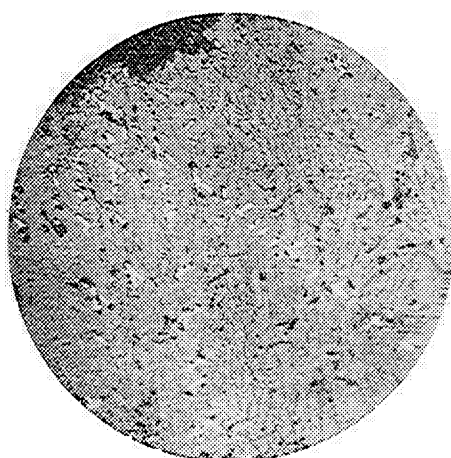


Photo. 7. Titanite, Perovskite and Silica.
 $\times 100$

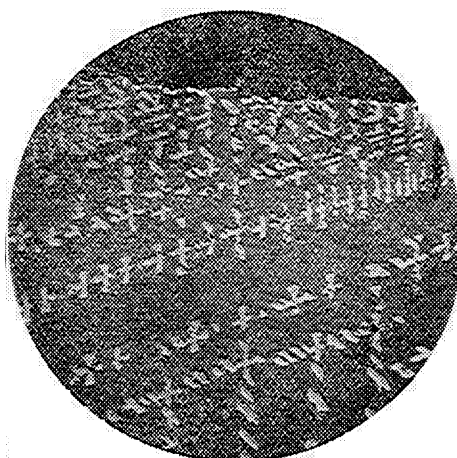


Photo. 8. Perovskite and Glass. $\times 100$

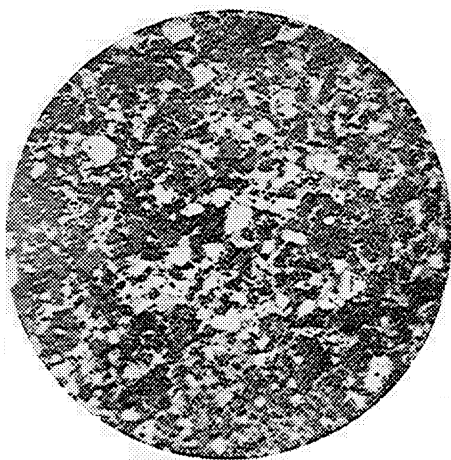


Photo. 11. Sintered Mixture of Perowskite and Silica. $\times 100$

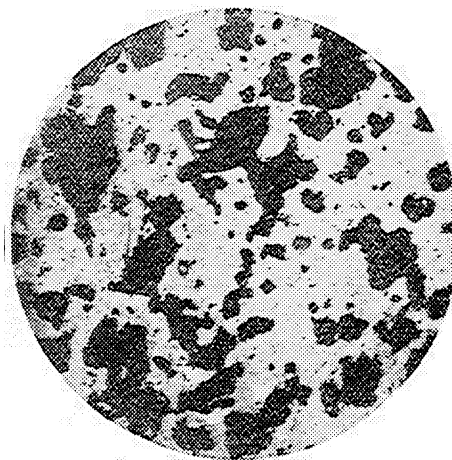


Photo. 12. Titanite from Perowskite and Silica. $\times 100$

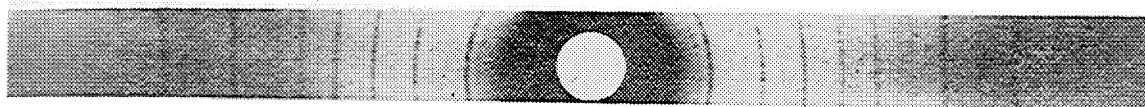


Photo. 3. Perowskite shown in Photo. 2.

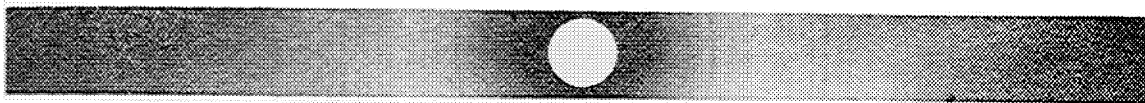


Photo. 5. Titanite shown in Photo. 4.

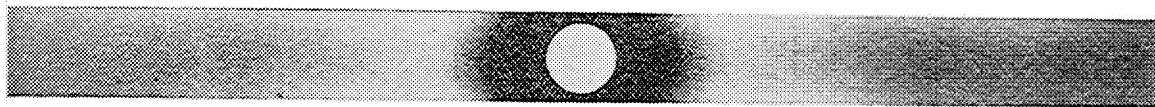


Photo. 9. Perowskite shown in Photo. 8.

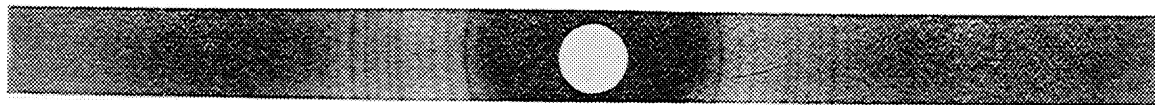


Photo. 10. Titanite shown in Photo. 6.

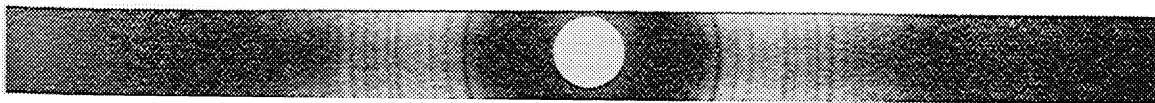


Photo. 13. Titanite shown in Photo. 12.

N.B. Anti-cathode: Copper.

Diameter of Camera: 75 mm.

II. Crystallization of Perovskite and Titanite from the Molten Titanite. As perovskite and titanite are frequently found in the crystallized mass of some silicates containing $\text{TiO}_2^{(1)}$, it is very important to study their crystallization for the investigation of the slag containing titanium formed in the smelting of the titaniferrous magnetic sand. From the standpoint of the physico-chemical conception, it is quite hard to take titanite as a component in the study of titano-silicates without making clear the phenomena of crystallization of perovskite and titanite from the molten titanite. The complete outline of the experimental results carried out by the present authors concerning this problem is as follows.

In the first place, about 2–10 gr. of titanite crystals were melted in a platinum crucible in a platinum wound furnace and the melt was solidified at various cooling rates, taking ordinary cooling curves at the same time. The solidified mass was then polished and examined under the reflected microscope. It was observed that the structure changed according to the condition of cooling, and in some cases, homogeneous products were obtained as is shown in Photo. 4, while in other cases, some light dendritic crystals were observed in it. Fig. 1 represents the cooling curves taken and Photos.

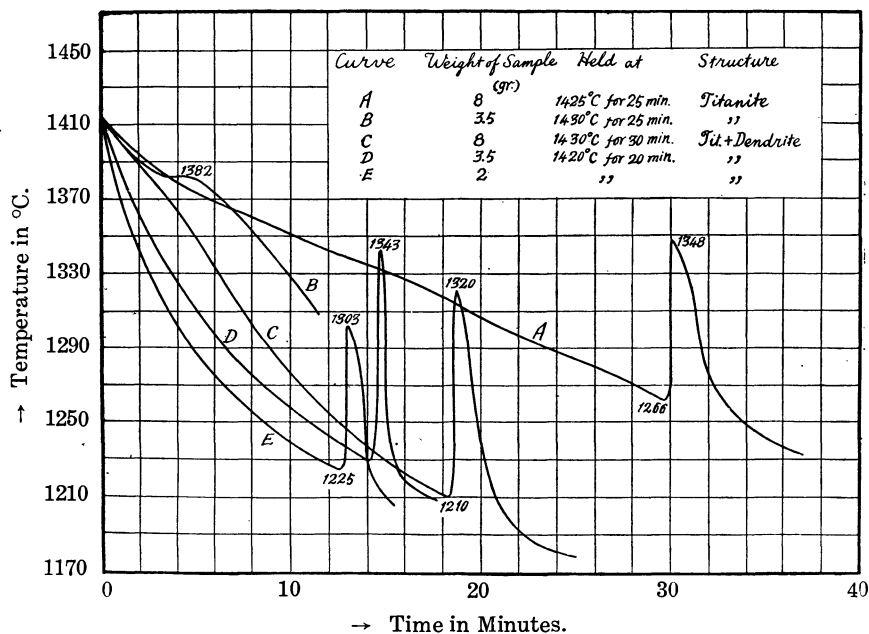


Fig. 1. Cooling Curves of Molten Titanite not Inoculated.

(1) Umezu and Kakiuchi, *J. Min. Inst. Japan*, **46** (1930), 994.

6 and 7 some of their structures. In the figure the heat treatment of the specimen prior to the beginning of the recording of the cooling curve and the structure of the specimen are demonstrated. By a careful study of the relation between the structure and its cooling condition represented in the curve, it has been concluded that the dendritic crystal above mentioned is formed when the melt supercools below ca. 1255°C .,⁽¹⁾ while when the melt solidifies above this temperature, the structure is always homogeneous. Hence, for the next experiment, the melt was carefully cooled to various temperatures and then it was quenched in ice water, together with the crucible, in order to obtain a structure consisting of the dendrite and glass, or glass only. In this experiment, 10 gr. of titanite were taken, heated to 1410°C . in a platinum crucible and melted. After keeping the melt at that temperature for about 10 minutes, it was cooled slowly to the following temperature and after certain number of minutes, it was quenched. The condition of the cooling of each melt and its subsequent structure were as follows :—

Time required for cooling from 1410°C . to the quenching temp. (min.)	Quenching temperature ($^\circ\text{C}$.)	Time kept for the quenching temp. (min.)	Structure
13	1360	45	Glass
15	1330	„	„
20	1310	„	„
23	1290	„	„
30	1280	„	Glass + Dendrite
35	1270	„	„
45	1255	30	„
60	„	60	„

From this experiment it is clear that the dendrite is formed when the melt is supercooled below 1280°C . and is held at these temperatures for certain minutes. The quantity of the dendrite formed is great at the surface of the quenched mass and becomes less toward the inside. The sample whose structure is shown in Photo. 8 was photographed by X-rays and the spectra thus obtained are shown in Photo. 9 which is in good agreement with those of Photo. 3. Hence the dendritic crystals shown in Photos. 6, 7, and 8 are determined as perowskite. Thus it is clearly established that perowskite does crystalize out from the molten titanite according to the cooling

(1) This temperature varies according to the condition, such as the quantity of the specimen, the surface area of the melt and the cooling rate etc. (see later.)

condition of the melt. When perovskite separates from titanite, SiO_2 is left in a free state and this is clearly seen in Photos. 6 and 7. In these photographs, the ground mass is titanite, the dendrite is perovskite and the grayish lamellae or flakes are thought to be SiO_2 . As the quantities of perovskite and SiO_2 are far less than that of titanite in these specimens, X-ray analysis has proved the existence of only titanite as is shown in Photo. 10. It has also been observed that the quantity of perovskite that separates from the melt increases as the cooling rate becomes slower and the degree of the supercooling becomes greater, but a structure consisting of only perovskite and SiO_2 and no titanite could not be obtained in any case, while a structure consisting of only titanite could easily be obtained when the melt did not supercool below ca. $1255\text{--}1280^\circ\text{C}$.

The apparatus for taking the cooling curves of the melt and that for quenching were as is shown in Fig. 2. The figure shows the platinum wound furnace in which the platinum crucible containing the melt is hung by a

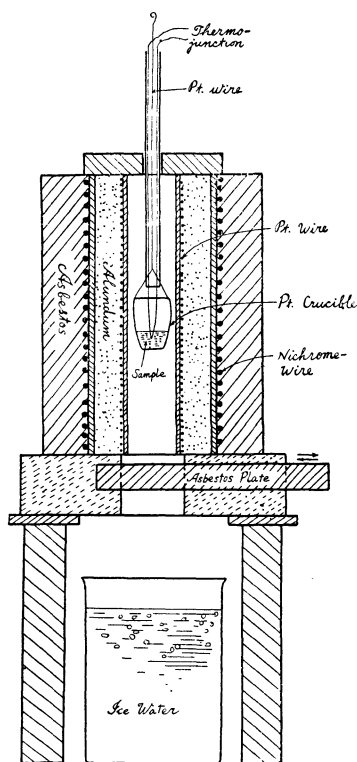


Fig. 2. Melting Furnace with Quenching Device.

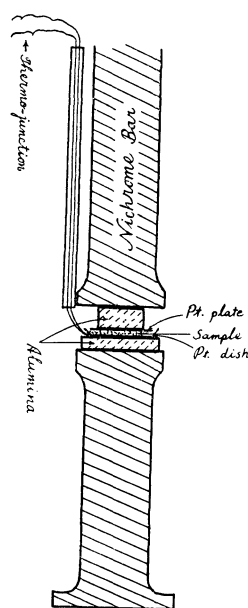


Fig. 3. Device for Heating with Pressure.

platinum wire. The hot junction of the thermo-couple dips in the melt at the point ca. 2—3 mm. apart from the surface of the melt. In the case of quenching the melt together with the crucible, the asbestos plate was pulled out and at the same time the crucible was unhooked to fall down into the ice-water in the beaker.

III. Stabilities of Perowskite and Titanite. From the results of the experiments in the preceding section and also from the general conception of the crystallization of silicates,⁽¹⁾ it may easily be supposed that titanite is more stable than perowskite in the system of titanite. The phenomena which support the above view have been observed in the course of the present experiment as follows:—

(1) When titanite was melted and then quenched from ca. 1390°C ., an uniform glass was obtained. By annealing the glass at a temperature higher than 800°C . only titanite crystal was observed but no perowskite. The titanite thus formed remained unchanged when it was heated as follows:—

Temp. ($^\circ\text{C}$.)	1160	1200	1255	1310	1365	1380
Time (Hr.)	2	2	1.5	2	2.33	2.5

(2) Although perowskite crystal was thrown into the molten titanite at about 1290 — 1380°C ., titanite crystal was formed and no perowskite was separated.

(3) When a sample having a structure such as is shown in Photo. 7, that is, having a structure consisting of perowskite, titanite and silica, was heated at about 1310°C . for several hours, no increase of the quantity of perowskite was observed, it always melted at a temperature of about 1390°C ., and after quenching the melt thus formed in ice-water, no trace of perowskite or silica was found. This is evidence that the specimen melted completely at about 1390°C . without leaving any perowskite or silica remaining. If titanite incongruently melts,⁽²⁾ the glass obtained by quenching as above mentioned should contain some crystals but this was proved not to be the case.

From these facts, it may be concluded that titanite is more stable than the mixture of perowskite and silica. In addition to this, positive proof of the above fact has been obtained by the present authors as follows. As above stated, by heating a mixture consisting of perowskite, titanite and silica in Photo. 7, no increase of perowskite or titanite was observed. But if titanite is more stable than the rest of the mixture, the quantity of titanite may be expected to increase by heating it at a high temperature. Hence in

(1) Doelter, loc. cit., Bd. I, 697.

(2) Eitel, loc. cit.

the next place, perowskite and silica were mixed together in equi-molecular proportion and the mixture was heated in a platinum crucible at about 1100—1300°C. in a furnace heated by carborundum bars for several hours. During the heating a massive bar made of nichrome was placed indirectly upon the content in the crucible as is shown in Fig. 3. The weight of the bar was about 7 kgr. The mixture thus heated changed more or less to titanite according to the following conditions.

Treatment	Structure
Heated at 1150°C. for 40 hours	A few titanite (Photo. 11) was formed.
Heated at 1150°C. for 40 hours and further at 1310°C. for 8 hours	Almost all the mixture changed to titanite (Photo. 12)

In Photo. 11, the brightly appearing mass is thought to be perowskite and the grayish part, titanite, and in Photo. 12, the grayish ground mass is titanite and the uncombined perowskite is seen in the middle portion of the ground mass, dark part being the void. That the grayish part in the last photograph is titanite was proved by the X-ray analysis as Photo. 13 shows.

Thus, it is decided that in the system of titanite, the mixture of perowskite and silica is less stable than titanite in the range of the temperatures experimented on.

IV. Melting Point of Titanite. As the molten silicate is apt to supercool more or less, its melting point is usually determined by the quenching method or by taking a differential heating curve of a very slowly heated specimen. But to the present authors, it seemed interesting to determine the melting points by cooling curve as is done with the metal. Therefore, the melting points of titanite and some other silicates which are apt to supercool were determined by cooling curves, throwing a nucleus⁽¹⁾ into the melt. The melt of titanite supercools as curves in Fig. 1 show, and the maximum point in each curve differs according to the cooling condition. By throwing glass, obtained by quenching the molten titanite, into the supercooled titanite, a very clear halting point was observed on the cooling curve as Fig. 4 shows. The quantity of glass was 0.01—0.02 gr. and it was thrown upon the melt at a position at a distance from the place where a hot junction of the platinum and platinum-rhodium thermocouple⁽²⁾ lies. The crystallization of the melt begins at once by the introduction of the nucleus and when the temperature of seeding is not too low, the horizontal part on the cooling

(1) As a nucleus, any solid substances may be availed, for instance, MgO, Al₂O₃ and glass have proved to be effective to excite the crystallisation of the molten silicates.

(2) The couple was calibrated with melting points of the following metals; Ag (961°C.), Au (1063°C.), Cu (1083°C.) and diopside (1391°C.).

Some Experiments with Perowskite ($\text{CaO} \cdot \text{TiO}_2$) and Titanite ($\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$).

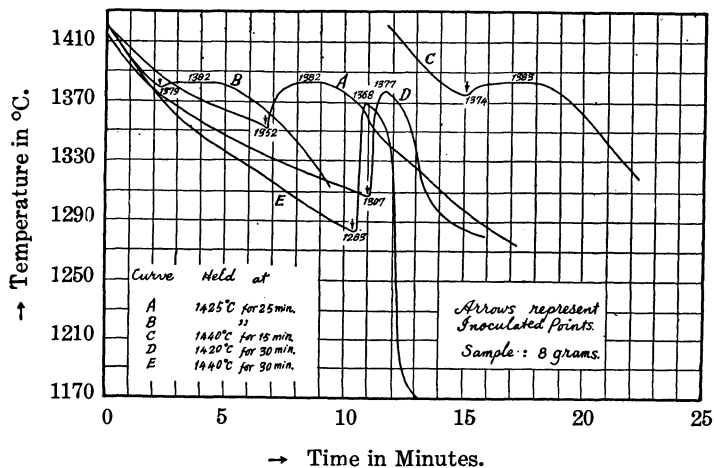


Fig. 4. Cooling Curves of Molten Titanite Inoculated.

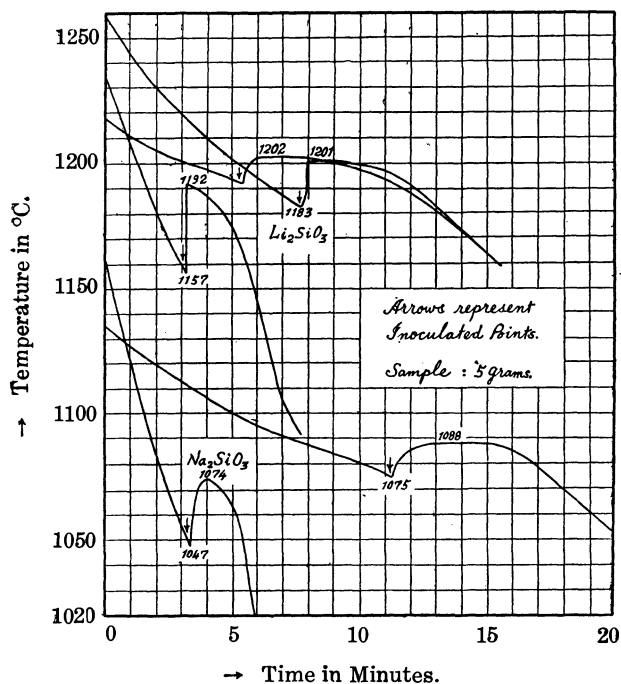


Fig. 5. Cooling Curves of Alkali silicates Inoculated.

curve lasts for several minutes, the temperature of which indicates the the melting point of titanite to be 1382°C . In the literature on the subject, the melting point of titanite is far lower than the above. On the cooling curves of molten titanite shown in M. Fukuda's paper (loc. cit.), there are found two points indicating the heat evolution of the melt. This is of course irrational and any of them can not be taken as its melting point.

Fig. 5 represents the cooling curves of Li_2SiO_3 and Na_2SiO_3 taken with seeding, which proves the superiority of seeding.

In conclusion, the present writers express their sincere gratitude to Prof. H. Shôji for the trouble of taking the X-ray photographs.

Summary.

1. Perowskite and titanite were synthesized from their respective components, using CaCO_3 instead of CaO .
2. Taking the X-ray spectra of these compounds as standards, the condition at which perowskite or titanite separates from the molten titanite has been fully determined.
3. Stabilities of these compounds have been determined by several methods.
4. Melting points of titanite and lithium and sodium silicates have been determined by cooling curves. Seeding was applied in this case and a very clear halting point has appeared in each case.

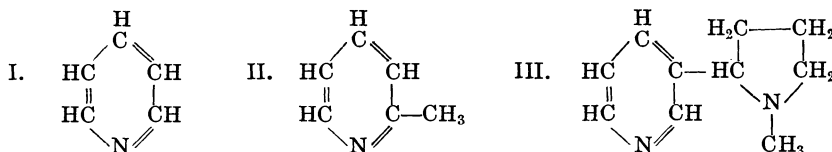
Research Institute for Iron, Steel and Other Metals,
Tôhoku Imperial University, Sendai.

DAS VERHALTEN DER PYRIDINGRUPPE BEI DER ELEKTROCHEMISCHEN OXYDATION. III. NICOTIN.

Von Moriaki YOKOYAMA.

Eingegangen am 28. Januar 1932. Ausgegeben am 28. April 1932.

Die Oxydation des Nicotins mit den üblichen chemischen Agentien ist bereits von einigen Forschern⁽¹⁾ durchgeführt worden, aber, soviel wir aus der Literatur entnehmen konnten, wurde das Nicotin (III) bisher noch nicht der Einwirkung des anodischen Sauerstoffs unterworfen. Nachdem nun in neuerer Zeit von uns die elektrochemische Oxydation von Pyridin⁽²⁾ (I) und α -Methyl-Pyridin⁽³⁾ (II) näher untersucht worden war, schien es uns besonders interessant, das Verhalten des Nicotins gegenueber dem Anodensauerstoff kennen zu lernen.



Beschreibung der Versuche.

4 cm³ Nicotin (Kahlbaum; sp. Gew. 1.0111) wurden in 175 cm³ 2-N. Schwefelsäure gelöst, und in einem Tondiaphragma an einer cylindrischen voroxydierten Bleianode mit 0.04 Amp./cm² anodischer Stromdichte unter starker Rührung oxydiert, wobei die Temperatur durch äussere Kühlung bei ca. 20°C. gehalten wurde. Die Kathode, ein Platinblech in 2-N. Schwefelsäure, umgab das Tondiaphragma. Die durchgeführte Strommenge betrug 16 F/Mol.

Der Anolyt färbte sich erst violett und wurde nach dem Durchsenden von etwa 8 F/Mol tiefrot. Aber die Farbe verblasste allmählich wieder während des weiteren Verlaufes der Elektrolyse; bei längerer Elektrolyse wurde der Anolyt schliesslich farblos.

-
- (1) Weidel, *Ann.*, **165** (1873), 328; Laiblin, *Ann.*, **196** (1879), 129; Cahour u. Etard, *Bull. Soc. Chim.*, [2], **34** (1880), 449; Blau, *Ber.*, **27** (1894) 2535; Pinner u. Wolfenstein, *Ber.*, **24** (1891), 61; Pictet, *Chem. Centr.* 1898 II, 677; Winterstein, *Z. Physiol. Chem.*, **100** (1917), 181.
 (2) Yokoyama und Yamamoto, dieses Bulletin, **7** (1932), 28.
 (3) Yokoyama, *ibid.*, **7** (1932), 69.

A. Die gasförmigen Reaktionsprodukte: Um ein Bild von der Art und dem Verlauf des Oxydationsprozesses zu erhalten, analysierten wir die in dem Anodenraum entwickelten Gase während der Elektrolyse nach der bei der elektrochemischen Oxydation von Pyridin erwähnten Methode⁽¹⁾ möglichst sorgfältig. Die folgende Tabelle zeigt einen typischen Versuch.

Table 1.

Stunden	Sauerstoff-coulom. (ccm.)	Anodengas (ccm.)	Prozente der aufgefangenen Gase (ccm.)			Stromausbeute (%)
			CO ₂	CO ₂	CO	
0.5	79.8	7.8	30.8	61.8	7.7	94.2
1	81.9	11.7	89.8	5.1	5.1	99.5
1.5	78.8	19.2	84.4	4.7	10.9	98.9
2	80.1	28.8	84.4	7.3	8.3	97.8
2.5	80.7	43.5	81.4	13.1	15.5	93.7
3	80.7	51.6	78.5	18.0	3.5	88.5
3.5	84.0	61.8	73.0	25.3	1.7	81.5
4	81.0	62.7	63.1	32.0	4.9	75.3
5	81.3	68.4	46.5	44.8	8.7	62.3
6	82.5	75.0	33.2	50.1	6.7	54.7
7	81.3	79.8	23.2	56.0	20.3	45.7

Wie aus der Tabelle ersichtlich ist, werden Kohlenmonoxyd und Kohlendioxyd erhalten und die Stromausbeute ist am Anfang fast theoretisch, sinkt aber im Verlauf der Elektrolyse ziemlich schnell. Aus diesen analytischen Daten kann man vielleicht so folgern, dass der Pyrrolidinring in der Nicotinmolekel zuerst aufgespalten wird. In dem Masse, wie sich dieser leichter oxydierbare Teil in den Molekeln verringert, geht der Verbrauch an elektrolytisch entwickeltem Sauerstoff zurück.

B. Die in Aether leicht löslichen Produkte: Nach beendeter Elektrolyse wurde der Anolyt unmittelbar mit Aether ausgeschüttelt. Die Aetherlösung hinterliess nach Entfernung des Aethers eine nach Ameisensäure riechende, gelb gefärbte Flüssigkeit. Nach dem Abdestillieren der Ameisensäure (Ausbeute: 0.03 gr. als Bariumformiat für einen Versuch) erstarrte die Flüssigkeit des Aetherrückstandes zu Krystallnadeln. Diese wurden auf Ton von anhaftenden Verunreinigungen (gelbliches Harz) befreit.

(1) Ibid.

Die Ausbeute war sehr gering; 0.035 gr. aus drei Einzelversuchen. Diese Substanz konnte durch zweimalige Umkrystallisation aus Wasser in weissen Tafeln erhalten werden. Die Krystalle reagierten sauer, zeigten sich leicht löslich in Wasser, Alkohol und Aether, färbten sich beim Erwärmen mit Essigsäureanhydrid gelbrot mit gelbgrüner Fluoreszenz, und schmolzen bei 131°C. Auf Grund dieser Beobachtungen muss der Stoff als Malonsäure betrachtet werden.

C. Die mit Wasserdampf flüchtigen Produkte: Die mit Aether extrahierte Lösung des Anolyten wurde hierauf mit Bariumcarbonat gegen Lackmus zur Abscheidung der Sulfationen neutralisiert. Das Filtrat vom Bariumsulfat und überschüssigen Bariumcarbonat wurde im Vakuum und im Stickstoffstrom zur Trockne eingedampft; die Vorlage enthielt zwecks Aufnahme der flüchtigen Gase etwa 100 cm³ verdünnter Salzsäure. Das Destillat wurde wieder zur Trockne eingedampft; es wurden so 0.83 gr. salzsaures Salz erhalten. Wir haben die Salze zunächst mit Goldchlorid versetzt, um so das unverändert gebliebene Nicotin abzuscheiden. Die hellgelbe Goldfällung, aus Wasser weiter umkrystallisiert, schmolz bei 192°C.⁽¹⁾

Aus den Mutterlaugen dieser Fällung liess sich beim Einengen kein einheitliches Produkt mehr abscheiden. Wir haben daher aus dieser Flüssigkeit mit Schwefelwasserstoff das Gold entfernt und die so wieder erhaltenen salzsauren Salze mit Platinchlorid versetzt; auf diese Weise gelang es uns, eine geringe Menge von Ammoniak im Form von Platinsalmiak (Ausbeute 0.15 gr. für einen Versuch) abzutrennen. Nach der Platinfällung haben wir wieder die Goldfällung durchgeführt, indem wir nach der Entfernung des Platins mit Schwefelwasserstoff die wieder erhaltenen salzsauren Salze mit Goldchlorid versetzten. So erhielten wir schliesslich gelbe nadelartige Krystalle, die sich als Methylamingoldchlorid (Ausbeute: 0.4 gr. für einzelne Versuche) erwiesen, dessen Analyse nach dem Trocknen über Schwefelsäure im Vakuum folgende Werte ergab.

0.1022 gr. Subst. gaben nach Glühen 0.0542 gr. Au. Gef.: Au = 53.03 % .

Ber. für CH₆NCl₄Au: Au = 53.14 % .

Das bei der Neutralisation von Schwefelsäure im Anolyt mit Bariumcarbonat entstandene Bariumsalz wurde zunächst mit Salzsäure auf dem Wasserbade behandelt, um überschüssiges Bariumcarbonat und die elektrolytisch entstandenen schwer löslichen dicarbonsauren Bariumsalze im Bariumchlorid zu verwandeln, und abfiltriert. Das Filtrat wurde nach dem Trocknen mit absolutem Alkohol behandelt. Unter den in Alkohol gelösten Substanzen

(1) Pinner, *Ber.*, **48** (1915), 181.

konnten wir Malonsäure leicht und Oxalsäure mit Wahrscheinlichkeit nachweisen.

D. Die mit Wasserdampf nicht flüchtigen Produkte: Der Rückstand vom Eindampfen war eine braune, zähe, harzartige Masse. Diese wurde mit einer kleinen Menge von heissem Wasser aufgenommen; auf diese Weise ging die Hauptmenge in Lösung, während ein wenig amorphe violette Substanz zurückblieb, deren Natur wir bis heute noch nicht infolge der geringen zur Verfügung stehenden Menge identifizieren konnten. Die nach der oben erwähnten Methode erhaltene Lösung wurde bei einer Temperatur von 80°C. mit einer gesättigten Lösung von Kupferacetat versetzt. Nun fiel ein blaugrünes, ziemlich schweres, undeutlich krystallinisches Kupfersalz (Ausbeute: 1.1 gr. für den einzelnen Versuch) aus, das nach dem Erkalten durch Filtration von der Lösung getrennt wurde. Das Kupfersalz wurde mit Schwefelwasserstoff in der Siedehitze zerlegt und lieferte nach dem Eindampfen eine gut krystallisierende Säure, die nach dem Entfärben mit Tierkohle und mehrmaligem Umkrystallisieren aus Wasser in farblosen, glänzenden, bei 229°C. schmelzenden Nadeln, welche beim vorsichtigen Erhitzen unzersetzt sublimierten, erhalten wurde.

Von kaltem Wasser wurde sie nicht, von heissem Wasser nur schwer gelöst. Eisenchlorid verursachte in der wässrigen Lösung keine Färbung, erst beim Erwärmen trat die für Nicotinsäure charakteristische Rotfärbung ein. Das Kupfersalz wurde nach dem Trocknen bei 100°C. einer Kupfer-Bestimmung unterworfen.

0.1321 gr. Subst. gaben nach dem Abrauchen 0.0339 gr. CuO.

Gef.: Cu = 20.62 % . Ber. für $(C_6H_4O_2N)_2$ Cu: Cu = 20.51 % .

Die von dem nicotinsauren Kupfer abfiltrierte Lösung wurde mit Schwefelwasserstoff entkupfert. Das Filtrat wurde in Vakuum im Stickstoffstrom zur Trockne eingedampft zur Entfernung der aus Kupferacetat entstandenen Essigsäure. Es hinterblieb nach dem Eindampfen ein rötlichbrauner Syrup, der in Wasser aufgenommen wurde. Der Lösung dieses Syrups setzten wir nach dem Filtrieren eine kalt gesättigte wässrige Pikrinsäurelösung zu um die darin enthaltene Base in Form des Pikrats abzuschcheiden. Anfangs erhielten wir das Pikrat als gelbes Produkt, das in der überschüssigen Base löslich war und daher dickes Oel ergab.

Erst wenn ein Ueberschuss von Pikrinsäure hingefügt wurde, löste sich der Niederschlag nicht mehr auf. Es bildete sich eine harzartige, schmutzigbraune Fällung (P), die sich bei ruhigem Stehen an den Wänden des Becherglases absetzte. Nach dem Einengen der milchigen darüber stehenden Flüssigkeit im Vakuum wurde zunächst braungelb gefärbtes Oel ab-

geschieden, das nach dem Erkalten zu einer krystallinischen Masse erstarrte. Dieser Körper, wiederholt aus Alkohol umkrystallisiert, stellte gelbe kleine prismatische Nadeln dar, die bei 150°–159°C. schmolzen. Das Pikrat wurde nach dem Trocknen der Analyse unterworfen, die folgende Werte ergab.

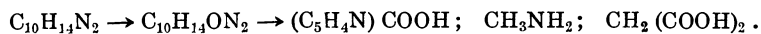
Subst. = 0.2836; CO₂ = 0.4304; H₂O = 0.0928 gr. Gef.: C = 41.39; H = 3.66 % .
Ber. für C₂₂H₂₀O₁₅N₈: C = 41.50; H = 3.17 %.

Nach diesen Beobachtungen handelt es sich wahrscheinlich um das Oxynicotin von Pinner und Wolffenstein.⁽¹⁾ Ueber die Natur des oben geschilderten, bräunlichgelben, amorphen Pikrats (P), dessen Schmelzpunkt 63°–68°C. war, konnten wir bis jetzt wegen Substanzmangels keine klare Vorstellung gewinnen.

Zur Kontrolle haben wir Pyridin- β -carbonsäure elektrolytisch oxydiert, da nach obigen Versuchen anzunehmen ist, dass die Abbauprodukte durch weitere Oxydation der Nicotinsäure entstanden sind. Wie bei der elektrochemischen Oxydation von Pyridin- α -carbonsäure⁽²⁾ erwähnt wurde, haben wir auch bei der Oxydation von Pyridin- β -carbonsäure Kohlendi- und monoxyd, Ameisensäure, Ammoniak, ein wenig Salpetersäure und kleine Menge von Mono-, Di- und Trimethylamin erhalten.

Schlussfolge.

Die elektrochemische Oxydation des Nicotins in verdünnter Schwefelsäure lieferte also hauptsächlich neben harzigen Produkten das oben erwähnte Oxynicotin, und bei der weiterer Oxydation dieses letzteren Nicotinsäure, Methylamin und Malonsäure. Der Haupt-verlauf der elektrochemischen Oxydation liess sich durch nachstehende Formeln wiedergeben.



Zusammenfassung.

(1). Bei der elektrochemischen Oxydation des Nicotins an der Bleidioxylanode in verdünnter Schwefelsäure wurden die folgenden Oxydationsprodukte erhalten: Ameisensäure, Malonsäure, Nicotinsäure, Oxynicotin, Methylamin, Kohlendioxyd, Kohlenmonoxyd und wahrscheinlich Oxalsäure.

(1) *Ber.*, **28** (1895), 460; **34** (1901), 2412.

(2) Dieses Bulletin, **7** (1932), 71.

(2). Nicotinsäure wurde bei den gleichen Bedingungen wie bei der Oxydation des Nicotins elektrochemisch oxydiert, und ergab Ameisensäure, Ammoniak, CO_2 , CO und kleine Mengen von Mono-, Di- und Trimethylamin.

(3). Der kinetische Verlauf der Gasabscheidung an der Anode während der Elektrolyse wurde analytisch verfolgt.

Technische Hochschule, Yokohama.

QUANTITATIVE SEPARATION OF WC FROM W_2C AND TUNGSTEN, AND THE CONDITIONS OF FORMATION OF THE TWO CARBIDES.

By Ichirô IITAKA and Yasuzo AOKI.

Received January 16th, 1932. Published April 28th, 1932.

Introduction.

Three different carbides, WC ($C = 6.12\%$), W_2C ($C = 3.16\%$), W_3C ($C = 2.12\%$), have been described of tungsten. H. Moissan and M. P. Williams^{(1) (2)} got W_2C by heating WO_3 or W with carbon in an electric furnace above $2000^\circ C$., WC was formed, in this case, only when excess of iron was added. This result has been written in many books and seems to be still generally believed. W. Hempel and P. Rucktäschel⁽³⁾ heated the compressed mixture of metallic powders of W with carbon black at high temperatures, but they did not find a carbide containing more carbon than 3.3 per cent. J. N. Pring and W. Fielling⁽⁴⁾ got W_2C by heating a carbon rod in WCl_6 gas above $1500^\circ C$. O. Ruff and R. Wunsch⁽⁵⁾ melted the mixed powders of tungsten and carbon in an electric furnace at above $2750^\circ C$. in vacuum or in the atmosphere of hydrogen. They could not get a higher carbide than WC . On quenching the molten mass containing both WC and W_2C in ice-water remained WC undecomposed. But when the quenching was done a little slowly some WC decomposed into W_2C and free carbon. They believed, besides, the existence of W_3C . M. R. Andrews⁽⁶⁾ heated

-
- (1) Moissan, *Ann. chim. phys.*, **7** (1896), 8,570; *Compt. rend.*, **116** (1893), 1225; *ibid.* **123** (1896), 13.
(2) Williams, *Compt. rend.*, **126** (1898), 1722; *ibid.* **127** (1898), 410.
(3) Hempel and Rucktäschel, *Z. angew. Chem.*, **17** (1904), 296, 321.
(4) Pring and Fielling, *J. Chem. Soc.*, **95** (1909), 1497.
(5) Ruff and Wunsch, *Z. anorg. Chem.*, **85** (1914), 292.
(6) Andrew, *J. Phys. Chem.*, **27** (1923), 270.

tungsten filament in the atmosphere of naphthalene etc. at above $1600^{\circ}K$. Free carbon deposited upon the filament and diffused into it. The electric resistance-composition curve proved clearly the existence of WC and W_2C but denied any higher carbides and W_3C . C. A. Matignon⁽¹⁾ got W_2C from WO_3 and carbon at $2130^{\circ}C$. A. Westgren and G. Phragmen⁽²⁾ observed that WC decomposes into W_2C and carbon on strong heating in a closed vessel. From these literatures we can conclude as following :

- (a) There is no carbide richer on carbon than WC.
- (b) Two carbides, WC and W_2C , were proved really to exist.
- (c) WC is formed only at very high temperatures or in presence of excess of iron. It decomposes into W_2C and carbon on cooling.
- (d) W_2C is most easily obtainable.
- (e) Ruff and Wunsch believed the existence of W_3C , but from insufficient evidence. Andrews showed, on the contrary, exactly that it does not exist. Other authors did not describe on it. So that it may be quite natural to deny its existence.

The samples prepared by previous investigators were all mixtures of W, WC, W_2C and C. They found total carbon, tungsten and free carbon by analysis and calculated the combined carbon. But they could not know the percentages of W, WC and W_2C . Their conclusions were, therefore, very ambiguous. In this paper a new analytical method to find directly the percentage of WC in the mixture was developed, and hence those of W and W_2C were also calculated. And the conditions of formation of the two tungsten carbides were found.

Experimental.

Preparation of Pure WC. The most reliable method ever known to get WC is to melt WO_3 or W with carbon in presence of excess of iron. The samples used in the experiments were prepared by the following two ways.

- (a) Powder of ferro-tungsten containing 80% of W was mixed with 2% of carbon black and melted in a carbon crucible. After cooling it was powdered and analysed.

Total carbon = 4.38; Free carbon = 0 % .

(Total carbon was determined in an ordinary way by combustion on adding CuO powder. A sample was taken in a platinum dish and the mixture of moderate HNO_3 and conc. HF was added. After the reaction was

(1) Matignon, *Compt. rend.*, **177** (1923), 1290.

(2) Westgren and Phragmen, *Nature*, **113** (1924), 122.

completed, the acids were removed by evaporation. The excess of ammonia was then added and the solution filtered through asbestos wool. Free carbon caught by asbestos was dried and analysed by combustion with oxygen.)

The sample was ground very finely in an agate mortar and the greater part of iron in it was extracted by warm hydrochloric acid (2 normal) on a water bath for 4 days. After the residue was washed with water and dried, it was subjected to magnetic separation. The residual sample containing about 10 per cent. of iron was heated at about 580°C . in the atmosphere of chlorine gas; it lost about 11 per cent. of its weight in this refining process. After washing with dilute ammonia and water it was dried and analysed.

Total carbon = 6.12; Free carbon = Trace; Fe = 0.16 % .

(b) Tungsten powder mixed with 7 per cent. of carbon black was heated in a carbon crucible at about 1800°C . The product was powdered and treated three times in the same way. The analysis of the final product was as follows.

Total carbon = 5.98; Free carbon = 0 % .

It was then ground very finely and heated at 580°C . in an atmosphere of chlorine gas, it lost 5.6 per cent. of its weight. It was washed by dilute ammonia and water and analysed after drying.

Total carbon = 6.10; Free carbon = 0.12 %; Fe = nil.

Considering from the results of the previous investigators and from the above analyses, it is certain that the samples prepared by the both processes (a) and (b) are pure WC.

A New Analytical Method to Separate WC Quantitatively from W_2C and W. *Principle:* Tungsten and W_2C react with chlorine gas and sublime at relatively low temperatures, but WC does not react until higher temperatures. This difference of reacting temperatures (or reaction velocities) was studied accurately and applied for the quantitative separation of WC from the others.

Experiment: The apparatus is shown in Fig. 1. Chlorine gas from a bomb was dried by passing through conc. sulphuric acid and introduced into the reaction tube. Care was taken each time to place the hot junction of the thermocouple, sealed in a thin porcelain tube, just above the center of the boat. When the required temperature was reached, the boat which had been kept at a cold part of the reaction tube was placed under the hot junction of the thermocouple. After a definite time (30 minutes) the heating current was cut off and the furnace was allowed to cool, still passing chlorine

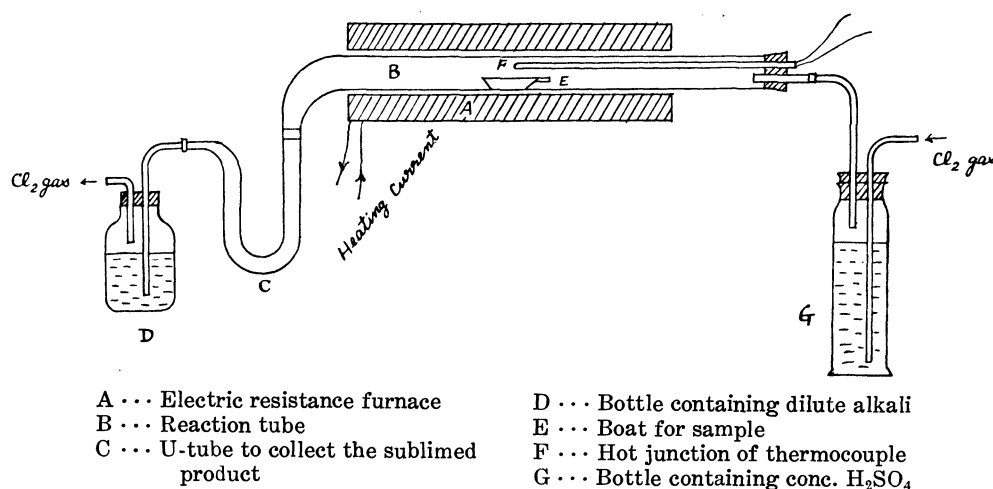


Fig. 1.

gas. The weight decrease of the sample was determined by weighing the boat before and after the experiment. The sublimed product was collected at C and D and analysed occasionally to check the result.

The Reaction of WC: Two samples (a) and (b) previously described were tested. The results are shown in Fig. 2. The decreases of weight expressed in percentage of the initial weight are taken as ordinates, while the temperatures as abscissae. The tungsten which was sublimed at $800^\circ C$. and collected together was 0.440 gr. This amount well coincides with 0.439 gr. of the weight decrease.

The Reaction of Tungsten: Two samples were tested. (a). Tungsten powder from E. Merck in Germany was reduced by hydrogen at $1000^\circ C$. (b). Powder of tungstic acid (WO_3) from E. Merck was reduced by hydrogen at $1000^\circ C$. The results are shown in Fig. 2.

The Reaction of W_2C : W_2C is most easily obtainable among tungsten carbides. Two kinds of samples were prepared. (a). Tungsten powder was mixed with 3.3 per cent. of carbon black and heated in a carbon crucible at about $1600^\circ C$. for

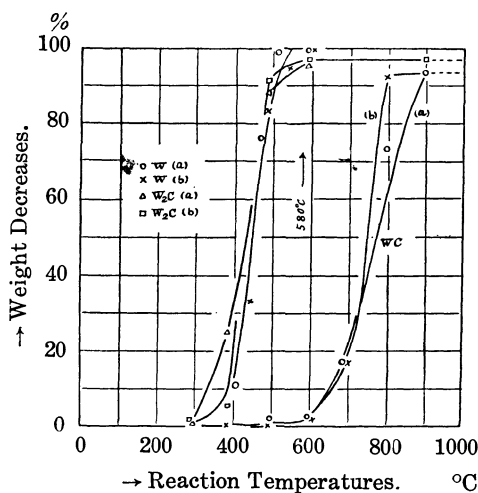


Fig. 2.

one hour. The greyish outer zone of the obtained mass was removed after cooling and the central part of yellowish brown was ground in an agate mortar. The elutriated and dried powder was reduced by hydrogen at 1000°C . (b). The second product had also greyish outer zone but its central part was coloured from green to blue. The blue part was collected and treated as (a). The results of analyses were as following.

(a) Total carbon = 2.41; Free carbon = 0 % .

(b) Total carbon = 2.61; Free carbon = 0 % .

These samples consist, no doubt, mainly of W_2C , but some WC and tungsten may also be contained. The results of experiments are shown in Fig. 2.

The Reaction of Carbon: The reaction residue of W_2C (in Fig. 2) at 900°C . was weighed as 2.61 per cent. of the initial weight and was found by analysis to contain 96.0 per cent. of carbon. It may be concluded, therefore, that both free and combined carbon are not lost when heated at such high temperatures in chlorine gas. In separate experiments carbon was also observed not to decrease its weight by heating up to 800°C . in chlorine gas. From the curves of Fig. 2 the following conclusions may be drawn.

1. WC does not react with chlorine under 600°C . The reaction begins at 600°C . and completes at about 800°C .

2. Tungsten reacts fairly at 400°C ., vigorously at 500°C . and the reaction completes under 550°C .

3. W_2C seems to react at a little lower temperature than tungsten and the reaction completes under 550°C .

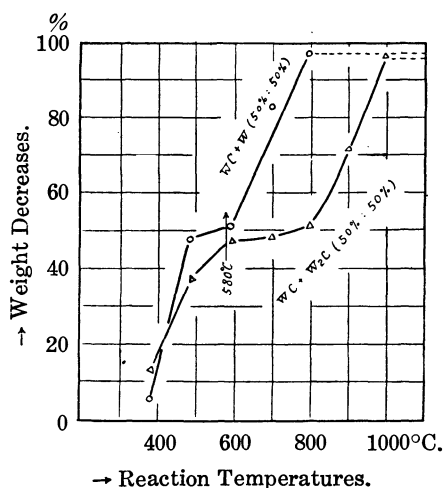


Fig. 3.

WC must, hence, quantitatively be separated from W_2C and tungsten on heating the mixture in chlorine gas at about 580°C . Some examples of analyses will be given in the next lines.

Example 1. $\text{WC} + \text{W}$ (50% : 50%)

Equal parts of samples of WC (b) and W (a) were mixed and ground in an agate mortar and heated in chlorine gas at various temperatures for 30 minutes. The results are given in Fig. 3. The decrease of weight at 580°C . is 51 per cent. This shows that the powder contains 49 per cent. of WC .

Example 2. WC+W (W = 92.6%)

595°C., 15 minutes.		Exp. 1	Exp. 2	Mean
	Decrease of weight, %	92.5	92.6	92.55

Example 3. WC+W (W = 5.20%)

595°C., 15 minutes.		Exp. 1	Exp. 2	Mean
	Decrease of weight, %	6.3	6.5	6.4

Example 4. WC+W₂C (50% : 50%)

The results are plotted in Fig. 3. The decrease of weight at 580°C. is 47 per cent. This shows that the powder contains 53 per cent. of WC.

Thus, it was confirmed that the new method is fairly reliable for the application on the quantitative separation of WC from the mixtures of tungsten carbides and tungsten. The percentages of W₂C and W may accordingly be calculated.

Conditions of Formation of the Two Tungsten Carbides (WC and W₂C). The mixed substances prepared under various conditions were analysed by the above analytical method and the conditions of formation of the two carbides were studied. The results are summarized in the next table. The last two samples were made by the following way. Tungsten powder mixed with 4 per cent. of carbon black was heated in a carbon crucible at various temperatures for one hour. The product was cooled very slowly, and its central part was ground in an agate mortar, elutriated and reduced by hydrogen at 1000°C.

Temperature	Total carbon	Free carbon	Note	WC	W ₂ C	W
1600°C.	2.41 %	0 %	Sample (a) assumed as W ₂ C	3.8 %	68.9 %	27.3 %
1600°C.	2.61 „	0 „	Sample (b) assumed as W ₂ C	2.5 „	79.0 „	18.5 „
2000°C.	2.64 „	0 „	—	21.6 „	42.0 „	36.4 „
2500°C.	4.40 „	0 „	—	42.3 „	57.2 „	0.5 „

The following conditions may be concluded from this table concerning the formation of carbides.

1. At low temperatures the one chiefly formed is hemiacbide (W_2C), monocarbide (WC) is formed only slightly and a considerable quantity of tungsten remains uncombined.

2. With rise in temperature the content of WC increases rapidly and that of uncombined tungsten decreases proportionally.

3. WC formed at high temperatures remains, for the greater part, undecomposed even after very slow cooling.

4. WC can be formed even when excess of iron is not present.

Research Laboratory, Mitsubishi Co. Ltd.,
Komagome, Hongô, Tôkyô.

ON TECTOQUINONE, THE VOLATILE PRINCIPLE OF THE TEAK WOOD.

By Kinzô KAFUKU and Keigai SEBE.

Received January 28th, 1932. Published April 28th, 1932.

It was Romanis,⁽¹⁾ who first studied the volatile constituents of the teak wood and isolated a crystalline component of quinonic nature which he named "tectoquinone". According to Romanis, this substance had a composition $C_{18}H_{16}O_2$, melted at $171^{\circ}C.$, and represented an anthraquinone derivative. His studies, which were made as early as 1887, were rather limited and it remained altogether unsettled whether his view for this substance was correct or not. The chemistry of this substance, somehow or other, was left untouched for nearly half a century ever since, when the present authors, happening to possess a quantity of reliable material, took up this old problem, and after a series of experiments, have at last succeeded in establishing the true nature of tectoquinone, the detailed account of which will be reported in the following.

If teak saw dust is extracted with ordinary organic solvents such as alcohol, acetone, petroleum ether, benzene, or toluene, about 5-9 % of a viscid semisolid resinous mass will be obtained. These extracts, on distillation with superheated steam, give a small amount of golden yellow needle-like crystals together with a large quantity of aqueous distillate. These crystals represent Romanis's tectoquinone, melt exactly at $171^{\circ}C.$, and show all the behaviours of tectoquinone as described by him. After repeated

(1) R. Romanis, *J. Chem. Soc.*, **51** (1887), 869; *Proc. Chem. Soc.*, **4** (1888), 116.

purifications, it became almost colourless, and its melting point rose to 174–175°C. This process is, however, extremely slow and uneconomical on account of the poor volatility of the substance in question, so the authors tried the other way, viz., the dry distillation. As a result, an oily distillate of strongly empyreumatic smell was obtained, from which tectoquinone could be isolated on standing for a while at a cool place. The yield of the crystalline component amounted to 0.5 % as referred to the weight of the starting material used.

These crystals also melted at 171°C. at first, and was of bright golden yellow colour, but after purifications they became colourless and melted at 175–176°C. By testing the mixed melting point of these crystals with those obtained by steam distillation, the authors could prove the identity of these two. Romanis, in his paper, expects tectoquinone to be structurally identical with retene quinone of the present day, which, at his time, was yet unknown, but such is not the case, now that retene quinone is already known which in every respect differs from tectoquinone. Moreover, according to the authors' analyses, the hydrogen content in tectoquinone turned out to be much smaller than corresponding to Romanis's proposed formula $C_{18}H_{16}O_2$, but to conform to $C_{15}H_{10}O_2$ or $C_{16}H_{12}O_2$. Furthermore, on treating tectoquinone repeatedly with excess of chromic acid, only one carboxylic acid resulted. This acid, on heating with soda-lime, yielded ordinary anthraquinone, whereas, if preliminarily reduced and then treated with soda-lime, it gave anthracene. Comparison of the derivatives of these carboxylic acids with those of anthraquinone and anthracene carboxylic acids led to the conclusion that tectoquinone should represent a β -alkylated anthraquinone. The following table shows the melting points of such derivatives as are related to the chemistry of tectoquinone. For the sake of brevity, the names "tectonic acid", "hydrotectonic acid" and "tectonene" are used to represent the carboxylic acid produced by oxidizing tectoquinone, that which is obtained by reducing the former, and the hydrocarbon which is formed by completely reducing tectoquinone, respectively.

Table

Substance	Melting Point
Tectoquinone	175–176°
Tectonic Acid	284–285°
Methyl Tectonate	164–165°
Ethyl Tectonate	147°
Tectonyl Chloride	146–147°

Table—(Concluded).

Substance	Melting Point
Hydrotectonic Acid	278–279°
Ethyl Hydrotectonate	135°
Hysrotectonic Acid Amide	278–279°
Tectonene	202–203°
α -Methyl-anthraquinone ⁽¹⁾	166–167°
Anthraquinone- α -carboxylic Acid.	293–294°
Anthraquinone- α -carboxylic Acid Methyl Ester.	293–294°
Anthracene- α -carboxylic Acid	245°
β -Methyl-anthraquinone ⁽²⁾	175–176°
β -Ethyl-anthraquinone	108°
Anthraquinone- β -carboxylic Acid.	285–292°
Anthraquinone- β -carboxylic Acid Ethyl Ester	147°
Anthraquinone- β -carboxylic Acid Chloride	146°
Anthracene- β -carboxylic Acid	245°
Anthracene- β -carboxylic Acid Ethyl Ester	135°
Anthracene- β -carboxylic Acid Amide.	280°
β -Methyl-anthracene.	200–207°

On reduction of tectoquinone with zinc and ammonia, a hydrocarbon, tectonene resulted, which in all probability is identical with β -methyl-anthracene. This hydrocarbon, on treatment with bromine, gave a difficultly recrystallizable dibromide, which after careful purifications melted at 166–167°C., agreeing with the melting point of meso-dibromo- β -methyl-anthracene. The reduction of tectoquinone by means of tin and hydrochloric acid in glacial acetic acid solution led to the formation of an unstable, difficultly crystallizable substance of undefined melting point, the analytical data agreeing with the composition $C_{15}H_{12}O$, probably identical with β -methyl-anthrone. The handiest product of reduction in this case is β -methyl-anthrahydroquinone, which can easily be obtained in form of its diacetate by boiling tectoquinone with zinc dust and anhydrous sodium acetate in acetic anhydride. This diacetate melts at 217°C. and its identity as such was proved by observing the mixed melting point with a known sample of the substance prepared from β -methyl-anthraquinone.

(1) O. Fischer, Sapper *J. prakt. Chem.*, [2] **83** (1911), 202.

(2) Kempf, *J. prakt. Chem.*, [2] **78** (1908), 257; Börnstein, *Ber.*, **15** (1882), 1821; Römer, Link, *Ber.*, **16** (1883), 695.

Nitration of tectoquinone afforded yellow-coloured crystalline needles melting at 263–265°C., the analyses agreeing with the composition $C_{15}H_9NO_4$, and was proved to be identical with 1-nitro-2-methyl-anthraquinone.

Aside from tectoquinone, a crystalline hydrocarbon, m.p. 199–200°C., was obtained from the oily distillate of dry distillation which was identified as β -methyl-anthracene, but the hydrocarbon melting at 94°C., which Romanis had reported to have isolated, could in no way be found in the present case. Also, attempts were made, to catch the oxy-derivatives directly from the wood by extraction with dilute alkali, but it proved altogether fruitless.

Experimental.

Extraction of Teak Saw Dust. 100 Gr. each of teak saw dust was extracted by means of 500 c.c. each of various solvents in the warm under reflux for six hours, and then the solvent evaporated, when 4.2 to 9.2 gr. of blackish semisolid resinous mass was left behind. All these residues melted around 100°C., and on cooling, coalesced into vitreous masses from which no crystalline component could be separated by filtration, recrystallization, or vacuum distillation. Only by prolonged distillation with superheated steam, however, it was possible to liberate the volatile crystalline substance, but it required too long a time to be practicable. The crystalline substance so obtained represented golden yellow needles with silky lustre, not uncontaminated with resinous impurities, but melted exactly at 171°C. as stated by Romanis. This was then purified by recrystallization from glacial acetic acid containing a little chromic acid so as to destroy resinous impurities present. After repeated treatments the melting point of the pure product rose to 174–175°C. and it became almost colourless. The yield of such pure product amounted to 0.3 % as referred to the whole weight of teak was dust used.

The Dry Distillation. A preliminary experiment with 100 gr. of teak saw dust has shown that the product of dry distillation was practically the same as in the case of Romanis. They came over in the following proportions :—

Tar heavier than water	12 %
Water and Water-solubles.	35 %
Carbonaceous Residue	33 %

The dark brown tar consisted for the most part of phenols and acids, the greater part dissolving in dilute alkali with evolution of heat. It was shaken with ether and dilute alkali several times and the neutral ethereal

solution remaining behind was evaporated on the water-bath. The gruel-like mass thus obtained, on cooling, congealed into a vitreous mass conglomerated with crystalline needles. This was then fractionally distilled under 7 mm. pressure, when the following fractions distilled over :—

Up to 150°	150–190°	190–235°	235°–265°	Residue
27.4 %	16.4 %	3.8 %	23.6 %	24.0 %

The first fraction represented a yellow-coloured mobile liquid with the peculiar odour of the teak wood, while the second fraction was more viscous than the former and on cooling deposited a small quantity of beautifully yellow-coloured needles. The third fraction was practically solid while the fourth was a dark brown viscous oil with a little crystalline precipitate in it. The third fraction was well-cooled and freed from the adhering oily matter by allowing it to drain on the porous porcelain plate, the crude crystals obtained in this way were recrystallized from glacial acetic acid to which a little active carbon had been added. The pure product thus obtained showed a melting point 175–176°C., and was proved to be identical with tectoquinone by 'mischproben'.

Thus, from 150 kg. of teak saw dust, about 400 gr. of such crystals were obtained, purified as above-stated, and were used in the experiments described below.

Properties of Tectoquinone. At ordinary temperatures, tectoquinone represents pale yellow needle crystals with silky lustre, which melt at 175–176°C., and boil at 215–220°C. under 4 mm. pressure. Under atmospheric pressures it sublimes but with decomposition. It is soluble in most organic solvents such as alcohol, ether, benzene, or acetone. It is also slightly soluble in hot water. It does not react with hydroxylamine or semicarbazide. When shaken with zinc dust and concentrated ammonia water, a deep blood-red colouration ensues, but it quickly discolours on exposure to the air and the original substance can be recovered unchanged from the solution. It is neither an alcohol nor a phenol, but represents an anthraquinone derivative. The colour reaction for phenanthrene was tried but with negative results.

Anal. Subst. = 0.0912, 0.0958; CO_2 = 0.2706; 0.2844; H_2O = 0.0400, 0.0418 gr.

Found: C = 80.80, 80.96; H = 4.87, 4.84 %. Calc. for $\text{C}_{15}\text{H}_{10}\text{O}_2$: C = 81.08;

H = 4.50%. Calc. for $\text{C}_{16}\text{H}_{12}\text{O}_2$: C = 81.38; H = 5.09 %.

The Crystalline Substance from Lower Fractions. From lower boiling fractions another crystalline component was obtained which after due purifications melted at 199–200°C. It boils a little lower than tectoquinone, viz., at 190–200°C. under 4 mm. pressure. It sublimes easily on heating it in

vacuo and gives bluish green tiny needles which fluoresce. It dissolves easily in hot alcohol or acetic acid from which it can be recrystallized. Its dilute solutions also fluoresce beautifully.

Anal. Subst. = 0.1042; CO_2 = 0.3550; H_2O = 0.0646 gr.

Found: C = 92.91; H = 6.89%. Calc. for $\text{C}_{15}\text{H}_{12}$: C = 93.75; H = 6.25%. Calc. for $\text{C}_{16}\text{H}_{14}$: C = 93.21; H = 6.78%.

On oxidizing this substance with strong chromic acid in glacial acetic acid, the same monocarboxylic acid as that obtained by the oxidation of tectoquinone, resulted. Furthermore, it showed no lowering of its melting point on admixture with the hydrocarbon obtained by the reduction of tectoquinone, and its other behaviours towards bromine or picric acid etc. agreed perfectly with those of the hydrocarbon above-mentioned. From these, it appears probable that this hydrocarbon must have been formed during the process of dry distillation from tectoquinone through the reducing action of carbonaceous matter, so that it should represent β -methyl-anthracene, although the analytical data are not satisfactory enough.

Oxidation of Tectoquinone. 12 Gr. of tectoquinone was dissolved in 300 c. c. of boiling glacial acetic acid and then a solution of 20 gr. of chromic acid in a suitable quantity of the same solvent was gradually added unto the boiling mixture and kept at boiling for two hours until the solution assumed a pure green colour. The whole solution was then cooled and the canary-yellow coloured needle crystals thereby precipitating were filtered on the pump. By evaporating the mother liquor, another crop of the same crystals was obtained, the total yield amounting to 13 gr. After several recrystallizations from glacial acetic acid it was observed to melt at 284–285°C.

Anal. Subst. = 0.0990; CO_2 = 0.2582; H_2O = 0.0318 gr.

Found: C = 71.13; H = 3.57%. Calc. for $\text{C}_{15}\text{H}_8\text{O}_4$: C = 71.4; H = 3.2%.

It is almost insoluble in ether, chloroform, benzene or water, but is moderately soluble in hot alcohol or acetic acid. On treatment with zinc dust and concentrated aqueous ammonia, it displays the characteristic blood-red colouration peculiar to anthraquinone derivatives, showing that the quinone grouping is left unaffected throughout the oxidative process.

Nextly, 2 gr. of the acid was intimately mixed with an equal amount of soda-lime and heated in a test-tube in a paraffin-bath at 290°C., when a sublimate was seen to form on the wall of the test-tube, which was collected, purified by recrystallization, and its melting point tested. It was observed to melt at 272–274°C. and showed no lowering of the melting temperature on admixture with a sample of pure anthraquinone. It follows that the

original carboxylic acid represents one of the two anthraquinone carboxylic acids.

The Chloride and the Amide of the Acid. In order to identify the acid, its chloride and amide were prepared in the following way. 3 Gr. each of the acid, phosphorus pentachloride were weighed out into a flask to which 50 c. c. of carbon disulphide was added and boiled for half an hour under reflux until the solid matter in the flask disappeared. Then the solvent and the excess of phosphorus pentachloride were distilled off and the residue was thrown into cold water. The crystalline solid separating thereby was filtered, dissolved in chloroform, the chloroform layer separated, dried and evaporated. The residue was then dried on the porous porcelain plate and finally recrystallized from glacial acetic acid. The chloride thus obtained melted at 146–147°C. It was readily soluble in alcohol, benzene, chloroform or carbon disulphide, but was only slowly acted on by cold water or alcohol. 2 Gr. of it was dissolved in 50 c. c. of benzene, a current of dry ammonia gas was passed through, the white precipitate forming thereby was filtered, washed with hot aqueous ammonia to remove the simultaneously produced ammonium salt, allowed to dry on the porous porcelain plate, and then recrystallized from benzene. The pure acid amide thus obtained melted at 278–279°C. It is very sparingly soluble in such solvents as alcohol, benzene, chloroform or carbon disulphide, and produces the characteristic blood-red colouration on treatment with zinc and ammonia water, showing that the quinonic structure is still left unchanged.

As for the melting points of anthraquinone carboxylic acids and their derivatives, we have in the literature, 293–294°C. for the α -acid,⁽¹⁾ and several data ranging from 285°C. to 292°C. for the β -acid,⁽²⁾ 147°C. for the β -acid chloride,⁽³⁾ 280°C. for the α -acid amide,⁽⁴⁾ and another datum that the β -acid amide melted higher than 280°C.⁽³⁾ With these data it is not yet sufficient to determine which of the two anthraquinone carboxylic acids represents tectonic acid—the acid obtained from tectoquinone, but it may certainly be regarded as likely that tectonic acid must be either the one or the other.

Preparation of Tectonic Esters.

(a) **Methyl Tectonate.** One gram of tectonic acid was dissolved in 50 c.c. of methyl alcohol, saturated with cold, dry hydrogen chloride, warmed

(1) Graebe, Leonhardt, *Ann.*, **290** (1896), 231.

(2) Liebermann, Bischof *Ber.*, **13** (1880), 49; O. Fischer *J. prakt. Chem.*, [2] **79** (1909), 558; Limpricht, *Ann.*, **309** (1899), 122.

(3) Liebermann, Glock, *Ber.*, **17** (1884), 889, 890.

(4) Graebe, Blumenfeld, *Ber.*, **30** (1897), 1116.

on the water-bath for thirty minutes, this treatment repeated again and again until all the solid dissolved away on warming, filtered while hot, and allowed to cool. In this way the methyl ester was obtained in form of pale yellow crystalline needles melting at 164–165°C. after purifications.

Anal. Subst. = 0.1254; CO_2 = 0.3304; H_2O = 0.0438 gr.

Found: C = 71.85; H = 3.88 %. Calc. of $\text{C}_{16}\text{H}_{10}\text{O}_4$: C = 72.18; H = 3.76 %.

(b) **Ethyl Tectonate.** The ethyl ester was prepared exactly in the same manner as described above, using ethyl alcohol in place for methyl alcohol. The crystalline ester so obtained melted after purifications at 147°C., the yield amounting to 2 gr. starting from 2 gr. of the acid.

Anal. Subst. = 0.1022; CO_2 = 0.2720; H_2O = 0.0410 gr.

Found: C = 72.60; H = 4.45 %. Calc. for $\text{C}_{17}\text{H}_{12}\text{O}_4$: C = 72.86; H = 4.28 %.

These esters are both very soluble in benzene or chloroform, also in hot alcohol or hot glacial acetic acid, and show the characteristic colour reaction on treatment with zinc and ammonia.

According to literature, the ethyl ester of anthraquinone- α -carboxylic acid⁽¹⁾ melts at 169°C., while that of the β -acid⁽²⁾ does at 147°C. The melting point of methyl ester of the α -acid is reported to be 189°C., which is decidedly higher than that of methyl tectonate. Thus, the identity of tectonic acid with anthraquinone-carboxylic acid looks very probable.

Reduction of Tectonic Acid.

(a) **Reduction with Zinc and Ammonia.** Two grams of tectonic acid was intimately mixed with 3 gr. of zinc dust and was added to 100 c. c. of 12 % aqueous ammonia under stirring and was warmed on the water-bath for two hours. The reaction mixture, which at first assumed an intense blood-red colour, gradually discoloured into pale greenish blue, and a remarkable fluorescence set in. It was filtered while hot, and allowed to cool. On acidification, a bulky precipitate separated out which gradually passed into crystalline needles. It was filtered on the pump, dried, and recrystallized from glacial acetic acid. The beautiful yellowish green crystals thus obtained, which amounted to 1.5 gr., melted at 274–275°C. This acid, if once transformed into its acid chloride and then restored to the original acid, then its melting point rises to 278–279°C., but never by repeating simple recrystallizations.

(1) Graebe, Blumenfeld, loc. cit.

(2) Liebermann, Glock, *Ber.*, **17** (1884), 889.

Anal. Subst. = 0.1400; CO_2 = 0.4148; H_2O = 0.0704 gr.

Found: C = 80.81; H = 5.58%. Calc. for $\text{C}_{17}\text{H}_{14}\text{O}_2$: C = 81.60; H = 5.60%.

The data on the melting point of anthracene carboxylic acid are as follows. 245°C . for anthracene- α -carboxylic acid,⁽¹⁾ $275\text{--}280^\circ\text{C}$. for the β -acid,⁽²⁾ 135°C . for the ethyl ester of the β -acid.⁽²⁾ These data for the β -acid and its ethyl ester are in good accord with the authors' substances, so the product in question, viz.—the hydrotectonic acid in the table—should be regarded as anthracene- β -carboxylic acid.

(b) **Reduction with Zinc and Acetic Anhydride.** 2 Gr. of tectonic acid was boiled with 30 c. c. of acetic anhydride together with 2 gr. of anhydrous sodium acetate and 4 gr. of zinc powder under reflux for 15 minutes. This mixture, which at first showed yellowish brown colour, soon clarified into bluish green fluorescent liquid and deposited a quantity of tiny orange-coloured needles, which after recrystallization from glacial acetic acid melted at $219\text{--}220^\circ\text{C}$.

Anal. Subst. = 0.1468; CO_2 = 0.3590; H_2O = 0.0358 gr.

Found: C = 66.70; H = 4.38%. Calc. for $\text{C}_{19}\text{H}_{14}\text{O}_6$: C = 67.45; H = 4.16%.

This substance, as dilute solutions in alcohol or acetic acid, fluoresces blue-green. On addition of alkali to the dilute alcoholic solution, it acquires red tinge, but it rapidly fades away to give anthraquinone- β -carboxylic acid. It has been reported that anthraquinone- α -carboxylic acid on treatment as above, gives the lactone of acetyl-anthrahydroquinone- α -carboxylic acid,⁽³⁾ whereas the acid under investigation led to the formation of a diacetate instead of a lactone, it follows that in the present case the carboxyl group must be attached to the β -position and not to α -.

Derivatives of Hydrotectonic Acid.

(a) **Anthracene.** 1.5 Gr. hydrotectonic acid was carefully mixed with 3 gr. of soda-lime and was heated in a test tube in the paraffin bath at 300°C . for half an hour, the crystalline sublimate thereby forming, was collected, recrystallized from alcohol, and resublimed in vacuo. It melted at $212\text{--}213^\circ\text{C}$. On mixing this substance with some pure specimen of anthracene, no depression of the melting point was to be perceived.

Anal. Subst. = 0.0944; CO_2 = 0.3233; H_2O = 0.0503 gr.

Found: C = 93.99; H = 5.48%. Calc. for $\text{C}_{14}\text{H}_{10}$: C = 94.38; H = 5.62%.

(1) Graebe, Blumenfeld, loc. cit.

(2) Börnstein, *Ber.*, **16** (1883), 2610; Limpricht, loc. cit., Liebermann, Bischof, *Ber.*, **13** (1880), 49.

(3) Scholl, Böttger, *Ber.*, **62** (1929), 625.

(b) **The Chloride and the Amide.** One gram of hydrotectonic acid was treated with 1 gr. of phosphorus pentachloride in 40 c. c. of carbon disulphide in the warm for half an hour, and finally the excess of the solvent and phosphorus pentachloride was distilled off, and the residue thrown into cold water. The brilliant golden yellow needles thereby crystallizing were filtered, dissolved in chloroform, dried on anhydrous sodium sulphate, chloroform evaporated, the residue was allowed to drain on the porous porcelain plate. It was found to melt at 172–173°C. This chloride is pretty stable, and is not acted on by cold water, but on being kept for a long time in the desiccator, or on being recrystallized from alcohol or acetic acid, it is liable to be transformed back into its mother acid or its ester, so it was quickly dried on the porous plate, and at such stage it was found to melt at 172–173°C. 0.5 Gr. of this acid chloride was treated with ammonia gas in benzene solution (100 c. c.) when a deposit in form of yellow leaflets separated out, which was filtered, washed with water and aqueous ammonia one after the other, and finally recrystallized from acetic acid. It represented beautiful yellow-green laminae and melted at 293°C. Its solutions in alcohol or glacial acetic acid showed a blue fluorescence.

Anal. Subst. = 0.1160; CO_2 = 0.3450; H_2O = 0.0536 gr.

Found: C = 81.12; H = 5.12 %. Calc. for $\text{C}_{15}\text{H}_{11}\text{NO}$: C = 81.45; H = 5.00 %.

The melting points of anthracene carboxylic acid amides are reported as 256° or 260°C. for α -acid amide,⁽¹⁾ and 293–295°C. for the β -acid amide.⁽²⁾ Thus the amide obtained here from hydrotectonic acid is most likely identical with anthracene- β -carboxylic acid amide.

The Reduction of Tectoquinone.

(a) **The Reduction by means of Zinc and Ammonia.** Four grams of tectoquinone and 8 gr. of zinc dust were stirred in aqueous ammonia (50 c. c. concentrated ammonia and 50 c. c. of water) on the water-bath under reflux, the blood-red coloured solution gradually bleached in course of two hours, which on cooling deposited a crystalline precipitate. The precipitate was filtered, redissolved in glacial acetic acid, refiltered while hot to get rid of excess of zinc dust and then allowed to cool. Thus, about 3 gr. of scaly crystals of yellowish green colour were obtained from the filtrate. After recrystallizations the substance melted at 202–203°C. with partial sublima-

(1) Dienel, *Ber.*, **39** (1906), 932; Graebe, Blumenfeld, loc. cit.

(2) Börnstein, loc. cit.

tion. It was difficultly soluble in cold glacial acetic acid but more soluble in the hot state. Its dilute solutions displayed a green-violet fluorescence.

Anal. Subst. = 0.0918; CO_2 = 0.3138; H_2O = 0.0541 gr.

Found: C = 93.20; H = 6.00 %. Calc. for $\text{C}_{15}\text{H}_{12}$: C = 93.75; H = 6.25 %.

Calc. for $\text{C}_{16}\text{H}_{14}$: C = 93.20; H = 6.80 %.

One gram of this hydrocarbon was dissolved in 40 c. c. of carbon disulphide to which a calculated amount of bromine (4 Br against 1 Mol.) in 10 c. c. of the same solvent was slowly added and stood still. In an hour the reaction was complete, and on evaporating off the solvent, about 1 gr. of a yellowish crystalline substance was left behind, which on recrystallization from glacial acetic acid gave needle crystals of bright yellow colour melting at 166–167°C., readily soluble in benzene, chloroform or carbon disulphide. Its dilute solutions also showed a green fluorescence.

Anal. Subst. = 0.1161; CO_2 = 0.2130; H_2O = 0.0287 gr.

Found: C = 50.05; H = 2.67 %. Calc. for $\text{C}_{15}\text{H}_{10}\text{Br}_2$: C = 51.48; H = 2.88 %.

Calc. for $\text{C}_{16}\text{H}_{12}\text{Br}_2$: C = 52.76; H = 3.32 %.

According to literature, the melting points for methyl anthracenes are stated to be 85–87°C. for the α -,⁽²⁾ and 202–207°C. for the β -modification,⁽²⁾ while as regards the mesodibromo-compounds we find 138–140°C.,⁽³⁾ 142–143°C.,⁽⁴⁾ and 148°C.⁽⁵⁾ for the β -derivative—these discrepancies seemingly arising from the difficulty of purification. In the present case, the mother hydrocarbon melts at 202–203°C., and the mesodibromide at 166–167°C. Thus it should be regarded as derived from β -anthracene, and the datum for the bromine compound as representing a purer specimen.

(b) **Reduction by means of Tin and Hydrochloric Acid.** To a boiling mixture of 4 gr. of tectoquinone, 10 gr. of granulated tin, and 100 c. c. of glacial acetic acid, 10 c. c. of concentrated hydrochloric acid was slowly added. After an hour, the reduction was complete, and the reaction mixture was filtered on the pump and the solution was poured into 500 c. c. of cold water. At first, an oily substance separated out which gradually coalesced into a crystalline deposit. This substance is very difficult to recrystallize and it was impossible to purify it so as to attain to the definite melting point. At any rate, it became indiffer-

(1) O. Fischer, Sapper, loc. cit.

(2) Kraemer, Spilker, Eberhardt, *Ber.*, **23** (1890), 3272; O. Fischer, Sapper, *J. prakt. chem.*, [2] **79** (1909), 558; Lavaux, *Ann. chim. phys.*, [8] **20** (1910), 445.

(3) Liebermann, *Ann.*, **212** (1882), 35.

(4) Börnstein, *Ber.*, **15** (1882), 1822.

(5) Weller, *Ber.*, **7** (1874), 1186; O. Fischer, *J. prakt. chem.*, [2] **79** (1909), 558.

ent to the colour reaction peculiar to the anthraquinone derivatives, and showed a decided tendency to return to the original substance on keeping for a long while, regaining the property to produce blood-red colouration on treatment with zinc and ammonia. Thus, it was so far purified by deposition from its dilute alcoholic solution by the addition of a large quantity of water, the milky fluid produced thereby being stood still for a length of time. By repeating such treatment five times, the melting of the resulting product rose to 80–90°C.

Anal. Subst. = 0.0938; CO_2 = 0.2982; H_2O = 0.0506 gr.

Found: C = 86.70; H = 6.00 %. Calc. for $\text{C}_{15}\text{H}_{12}\text{O}$: C = 86.54; H = 5.77 %.

It dissolves easily in alcohol, benzene or glacial acetic acid, but not much in alkalis. This feature of solubilities together with the tendency of retransforming into the original substance, as well as the analytical data, agree with the properties of methyl-anthrone. As to the melting point of methyl-anthrone, there are reported.

3-methyl-anthrone-9 80–84°C.,⁽¹⁾ 86°–88°C.,⁽²⁾ 101°C.⁽²²⁾

2-methyl-anthrone-9 103°C.⁽³⁾

According to Barnett and Frederick, the anthrones from β -methyl-anthraquinone represent a mixture of 3-methyl-anthrone-9 and 2-methyl-anthrone-9, and the separation of these two from one another by means of simple recrystallizations is practically impossible.

(c) **Reduction by means of Zinc and Acetic Anhydride.** One gram of tectoquinone was dissolved in 20 c. c. of acetic anhydride to which 2 gr. of zinc dust and 3 gr. of anhydrous sodium acetate were added and the whole was boiled under reflux for an hour, when the brownish yellow colour of the initial mixture faded almost completely and a slight fluorescence became perceptible. After cooling, it was slowly poured into cold water and kept still. The greenish yellow leaflets separating out therefrom, after recrystallizations from alcohol, showed a melting point 216–217°C., agreeing with the data for β -methyl-anthra-hydroquinone diacetate.⁽⁴⁾ It dissolved readily in alcohol or acetic acid in the warm, and the solutions fluoresced blue green.

(1) Liebermann, Manlock, *Ber.*, **38** (1905), 1792.

(2) Padova, *Ann. chim. phys.*, [8] **19** (1910), 395.

(3) Barnett, Frederick, *J. Chem. Soc.*, **1929**, 1755.

(4) Liebermann, *Ber.*, **21** (1888), 1172.

Anal. Subst. = 0.1116; CO_2 = 0.2964; H_2O = 0.0522 gr.

Found: C = 72.44; H = 5.17 %. Calc. for $\text{C}_{19}\text{H}_{16}\text{O}_4$: C = 73.05; H = 5.20 %.

This substance, on treatment with alcoholic potash furnished a blood-red coloured solution which discoloured in course of time to be restored into tectoquinone again. Such tectoquinone was observed to melt at 176–177°C., and seemed to represent the substance of the highest purity as far as the authors' experiments are concerned.

The Nitration of Tectoquinone. Into a cold mixture of 20 c. c. concentrated sulphuric acid and 15 c. c. concentrated nitric acid, 2 gr. of tectoquinone was slowly introduced in small portions with constant stirring and cooling. After all the crystals dissolved away, the whole mass was warmed on the water-bath when a yellow crystals of the nitro-compound separated out. This nitro-compound was only sparingly soluble in most of the organic solvents and could only be recrystallized from a large volume of hot glacial acetic acid. After five consecutive recrystallizations it was observed to melt at 262–265°C. with decomposition.

Anal. Subst. = 0.1047; CO_2 = 0.2542; H_2O = 0.0327 gr.

Found: C = 66.26; H = 3.46 %. Calc. for $\text{C}_{15}\text{H}_9\text{NO}_4$: C = 67.41; H = 3.37 %.

The melting point and the analytical data agree with 1-nitro-2-methyl-anthraquinone.⁽¹⁾ An impure 1-oxy-2-methyl-anthraquinone of m. p. 170°C. could be obtained from this nitro-compound by treatment with tin and hydrochloric acid and subsequent diazotization etc.

Summary.

(1) Tectoquinone, the volatile crystalline ingredient of the teak wood, which was isolated by R. Romanis in 1887, represents β -methyl-anthraquinone.

(2) Tectoquinone, on oxidation, gives tectonic acid, which is identical with anthraquinone- β -carboxylic acid.

(3) Tectoquinone, on reduction, gives a hydrocarbon 'tectonene', which, on examination, was proved to be β -methyl-anthracene.

(4) Tectoquinone, on treatment with zinc and acetic anhydride, gives β -methyl-anthra-hydroquinone diacetate melting at 216–217°C., which is very easy to purify and thus may be used for the purpose of identifying tectoquinone.

(1) Römer, Link, *Ber.*, **16** (1883), 697; Holdermann, *Ber.*, **39** (1906), 1257.

(5) β -Methyl-anthra-hydroquinone diacetate, on treatment with alcoholic potash and subsequent exposure to the air, regenerates tectoquinone of highest purity, melting at 176–177°C.

The Department of Industry,
Government Research Institute of Formosa, Taihoku.

ELECTROLYTIC REDUCTION OF ALKYLPHthalIMIDES. II. PHTHALIC ANHYDRIDE.

By Buhei SAKURAI.

Received February 8th, 1932. Published April 28th, 1932.

Phthalic anhydride was reported by J. Wislicenus⁽¹⁾ to give several reduction products, such as diphtalyl, phthalide, hydrodiphtalyl and dihydrophthalyl lactonic acid, when reduced with glacial acetic acid and zinc, while A. Reiser⁽²⁾ obtained only diphtalyl lactonic acid by reducing phthalic anhydride with a mixture of potassium chloride, alcohol and zinc dust. On comparing these reduction products produced by a purely chemical method with those obtained by electrochemical reduction of phthalimide reported in the present writer's previous communication,⁽³⁾ it was deemed very interesting to study how reduction of phthalic anhydride really takes place electro-chemically.

In an experiment conducted with an ammonium carbonate solution using lead as the cathode, reduction of phthalic anhydride to phthalide was observed to take place smoothly at high temperatures. Evidently phthalic anhydride changed into ammonium phthalate before it was reduced, and the catholyte remained always slightly alkaline till the end of the electrolysis. Besides lead, metals having moderate overvoltage for hydrogen, such as nickel and copper could be used with nearly the same efficiency.

Reduction in a sodium bicarbonate solution was accomplished with difficulty. Electrolysis was conducted by passing a constant current of carbon dioxide into the catholyte with the object of preventing it from becoming too alkaline. At comparatively low temperatures such as 30°–40° C., a small quantity of phthalide was produced as the reduction product, which gradually decreased as the temperature rose, till at last at tempera-

(1) *Ber.*, **17** (1884), 2178.

(2) *Ber.*, **46** (1913), 1484.

(3) This Bulletin, **5** (1930), 184.

tures above 70°C., the reduction completely came to an end. The reason why the reduction does not proceed at high temperatures is not difficult to find, if we suppose that too strong alkalinity of the catholyte is unfavourable to the reduction. Experimentally to confirm whether this supposition be true or not, electrolysis of a sodium or potassium phthalate was once by itself and once by constantly neutralizing a greater part of alkali set free in the catholyte with hydrochloric acid. As was expected, no reduction product was formed in the former case, while in the latter phthalide was obtained with a moderate yield.

Reduction of phthalic anhydride in an acid solution was also undertaken, but all efforts to procure the reduction products turned out fruitless.

Throughout all experiments the reduction product was always found to be phthalide, and neither oxyphthalide nor other reduction products chemically got by Wislicenus could be isolated. So it was attempted to obtain reduction products other than phthalide, by controlling the temperature and the current density and also by using many different metals as the cathode. All these trials were, however, made in vain, producing in no case, any other reduction product.

Electrolysis was also carried out with the bath previously mixed with some phenyl-hydrazine to see if some intermediated product such as oxyphthalide could be isolated in some form combined with the hydrazine. This expectation was also betrayed, nothing but α -phthalyl benzyl hydrazine been obtained.

Experimental.

1. Ammonium Carbonate Solution as the Catholyte. Experiment was conducted under the following conditions:

Anode: lead; Anode solution: a saturated ammonium carbonate solution; Cathode: lead (200 sq. cm.); Catholyte: 40 c.c. of saturated ammonium carbonate solution + 80 c.c. of alcohol + 10 gr. of phthalic anhydride; Current density: 2 amp./100 sq. cm.; Temperature: 75°—80°C.

After an hour's electrolysis the catholyte which always remained slightly alkaline was acidified with hydrochloric acid and evaporated to drive off alcohol, whereupon about 2.3 gr. of the white tabular crystal of phthalide separated out. The yield is calculated to be 25%. It was increased to 85% by 3 hour's electrolysis and to 96% by continuing it still 2 hour's longer.

2. Ammonium Phthalate Solution as the Catholyte. A solution containing 10 gr. of ammonium phthalate in 100 c.c. was taken as the catholyte and 5% ammonia water as the anolyte, and electrolysis was carried out for 2 hours under the conditions as in 1. On cooling the catholyte after acidify-

ing it with hydrochloric acid, about 6 gr. of phthalide were isolated. The yield corresponds to 90% of the theoretical.

3. Ammonium Acetate Solution as the Catholyte. Five grams of phthalic anhydride dissolved in a mixture of 40 c.c. of 10% ammonium acetate and 80 c.c. of alcohol was electrolysed in an analogous manner as in 1, taking 10% ammonium acetate solution as the anolyte. The yield of phthalide was found to be 33%.

4. Sodium Bicarbonate Solution as the Catholyte. It was first supposed that the use of a sodium bicarbonate solution would be suitable for the reduction of phthalic anhydride, as the alkalinity of the solution might be kept nearly unaltered simply by passing carbon dioxide to the catholyte. But it soon became clear that such was not really the case. For phthalic anhydride is hardly soluble in a saturated sodium bicarbonate solution, and if alcohol is added to the catholyte in order to increase the solubility of the anhydride, it decreases that of the bicarbonate. Elevation of temperature to the neighbourhood of 75°C. increases the solubility of the anhydride, but this makes the catholyte strongly alkaline in spite of a constant influx of carbon dioxide. In short, to keep phthalic anhydride dissolved in a saturated sodium bicarbonate solution without greatly increasing the alkalinity of the solution was hardly practicable, and consequently the electrolytic reduction of phthalic anhydride with this solution produced only a very small quantity of phthalide at 20°–30°C., and no phthalide at 75°C.

5. Alkali Phthalate Solution as the Catholyte. Soon after electrolysis was commenced, the catholyte became strongly alkaline, though carbon dioxide was constantly passed into it, and perhaps for this reason no reduction took place. When, however, the same electrolysis was repeated by constantly dropping two normal hydrochloric acid into the catholyte so as to keep it always slightly alkaline, phthalide was obtained with 35% yield.

6. Acid Solution as the Catholyte. Electrolytic reduction of phthalic anhydride in an acid solution was attempted by using sulphuric, hydrochloric or acetic acid, concentrated and dilute. But in no case could a substance deemed to be a reduction product be procured.

The writer takes this opportunity warmly to thank Professor Motooki Matsui of Kyoto Imperial University, at whose suggestion the work was carried out.

Chemical Institute, Osaka Women's College,
Sumiyoshi, Osaka.

Feb. 2nd, 1932.

ELECTROLYTIC REDUCTION OF ALKYLPHTHALIMIDES.

III. REDUCTION OF PHTHALIC ANHYDRIDE.

By Buhei SAKURAI.

Received February 8th, 1932. Published April 28th, 1932.

In the previous experiments⁽¹⁾ it was found that for electrolytic reduction of phthalates electrolysis must be conducted at a higher temperature using a solution not too alkaline. Now with the object of making these relations still clearer an experiment was first carried out to see the influence of temperature on the reduction reaction.

As the catholyte a 5% ammonium phthalate solution was taken, and this was electrolysed, on a constant agitation, with a lead cathode by passing a current of 1.5 amperes for 100 sq. cm. of the cathode. Lead was also chosen as the anode, which dipped to the anolyte consisting of 5% ammonia water. During the course of electrolysis the bath was dipped in water to keep its temperature constant, and when the temperature began to rise 5 degrees higher than the constant temperature, the electric current was cut off for a while to cool the bath again to the constant temperature. The material yields of phthalide after an hour's electrolysis were as follows ;

Temperature	50 — 55°	60 — 65°	70 — 75°	80 — 85°
Yield %	very small	6	80	90

Smooth reduction is thus seen to take place only at temperatures higher than 70°C.

Next, to know the effect of the alkalinity of the solution on the reduction, the pH value of the catholyte was constantly observed using Shibata's electrometric titration apparatus prepared by Shimadzu & Co. Three different phthalic anhydride solutions, as shown in the following table, were electrolysed for 90 minutes by passing a current of carbon dioxide at the rate of 60 c.c. per minute, and during the whole course of electrolysis, the pH value in the catholyte was observed at intervals of ten minutes. The results are shown in Tables 1 and 2.

(1) This Bulletin, 7 (1932), 128.

Table 1.

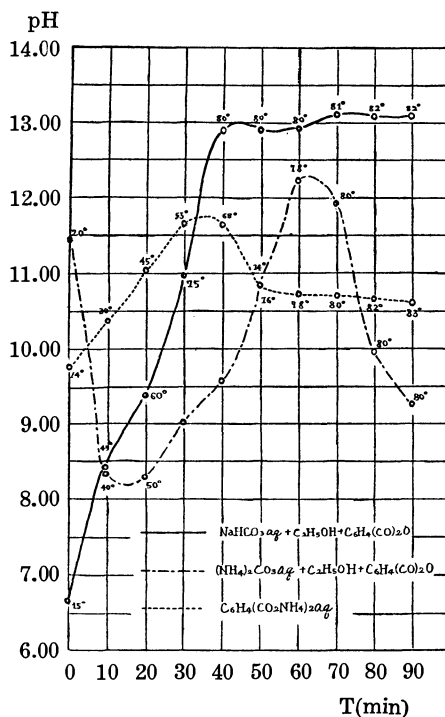
Catholyte	Cathode	Anolyte	Anode	Current density Am./100 sq. cm.	Temp. max.	Time min.	Yield % of phthalide
Satur. NaHCO_3 60 c.c. Alcohol 60 c.c. Phthalic anhyd. 5 gr.	} lead	Saturated NaHCO_3	lead	1.5	82	90	0
Satur. Am_2CO_3 60 c.c. Alcohol 60 c.c. Phthalic anhyd. 5 gr.							
Water 120 c.c. Am phthalate 5 gr.							
	} lead	Saturated Am_2CO_3	lead	1.5	80	90	50
	} lead	5% ammonia water	lead	1.5	83	90	75

Table 2.

	Sodium bicarbonate		Ammonium carbonate		Ammonium phthalate	
Time of electrolysis (min.)	Temp.	pH	Temp.	pH	Temp.	pH
0	15	6.33	20	11.43	14	9.70
10	45	8.39	40	8.28	30	10.35
20	60	9.28	50	8.26	45	11.00
30	75	10.98	65	9.04	55	11.59
40	80	12.85	73	9.54	68	11.61
50	80	12.80	76	10.85	74	10.83
60	80	12.82	78	12.24	78	10.72
70	81	13.00	80	11.96	80	10.68
80	82	13.00	80	9.96	82	10.62
90	82	13.02	80	9.33	83	10.58

Change of pH value in the course of electrolysis may be traced more clearly in the following figure.

In the electrolysis of the sodium bicarbonate solution, the pH value rapidly increased with temperature, and at temperatures favourable for reduction, the cathode solution became strongly alkline in spite of a constant influx of carbon dioxide gas. The reason phthalic anhydride could not be reduced well in this solution is thus clearly seen.



The ammonium carbonate solution behaves quite differently. In the first stage, the pH value decreases, and from 40°C. upward increases attaining a maximum value of 12 at 78°C. From this point it begins again to decrease, perhaps owing to the evaporation of ammonia, and in this manner the catholyte becomes very suitable for reduction of phthalic anhydride at the temperature, as well as in the condition of the solution.

In the case of ammonium phthalate, change of the hydrogen ion concentration under temperature is comparatively small and gradual, and at the temperatures favourable for reduction, the pH value is always found to be less than 11.

From the above results, that pH value of the electrolytic bath suitable for reduction of phthalic anhydride may roughly be estimated to lie between 10.5–12.

The writer's warm thanks are due to Professor Motooki Matsui of Kyoto Imperial University, at whose suggestion this work was carried out.

Chemical Institute, Osaka Women's College,
Sumiyoshi, Osaka.

Feb. 2nd, 1932.

SORPTION OF GASES BY SILICA GEL.

By Jitsusaburo SAMESHIMA

Received March 23rd, 1932. Published April 28th, 1932.

In the preceeding paper of the author⁽¹⁾ the measurement of sorption amounts and velocities of ammonia by silicic acid minerals were described. In the present paper the results of measurements are reported on silica gel prepared in vitro.

The silica gel has been prepared in the following manner. Fifty grams of pure sodium silicate from Merck was dissolved in 320 grams of water obtaining a solution of specific gravity 1.10. The solution was mixed with 300 c.c. of 3 normal sulphuric acid and the gel allowed to set. It was then washed with water thoroughly to remove the sodium and sulphate ions. The gel was dried by allowing a long time in an open vessel at the room temperature.

The dry gel thus prepared was dehydrated by evacuating and heating. The dehydrated substance was put in the measuring apparatus of sorption. The preparation of gases, the apparatus and the method of measurements were already described in the former papers.⁽²⁾ The experiments were conducted at 25°C. and under about one atmospheric pressure of gas.

Sorption of Ammonia. The silica gel was dehydrated by evacuating and heating to 300°C. for 30 minutes. By this treatment, 0.6852 gr. of air dry gel gave 0.3668 gr. of dehydrated substance. The amount of water evaporated is, therefore, 46.47 %. The velocity and the amount of sorption of ammonia by this dehydrated silica have been measured. The results are given in Table 1.

In this table, the first column indicates the time in minutes after the contact of gel to ammonia, the second the pressure of ammonia, and the third the volume of ammonia sorbed at 25°C. by 1 gr. of the dehydrated gel in c.c. reduced at 0°C. and 760 mm. pressure. The gel, thus, sorbed about 46 c.c. of ammonia at 25°C. and under 1 atmosphere.

(1) Sameshima, this Bulletin, **6** (1931), 165.

(2) Sameshima, this Bulletin, **2** (1927), 2; **4** (1929), 97; **5** (1930), 173.

Table 1. Sorption of NH_3 by Silica Gel.

Time in min.	Pressure of gas in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of gel in c.c.
0.5	762.5	29.00
1	762.5	35.14
2	762.5	40.19
5	762.5	43.29
10	762.4	43.64
20	762.3	43.96
185	760.8	44.64
1470	756.6	45.26
7315	761.3	45.87
17370	752.8	46.01
33225	750.3	46.26
77760	746.9	46.53

Now the gel was made to desorb the ammonia by pumping the gas and heating to 150°C. Then the second measurement has been done on this desorbed gel. The results are shown in Table 2.

Table 2. Second Sorption of NH_3 by Silica Gel.

Time in min.	Pressure of gas in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of gel in c.c.
0.5	759.2	29.93
1.17	759.2	37.30
2	759.2	41.11
4	759.2	42.94
6	759.2	43.20
10	759.2	43.39
15	759.2	43.52
30	759.2	43.76
50	759.2	43.96
135	758.7	44.27
280	758.9	44.48
1585	757.8	45.02
11520	765.6	45.85

Sorption of Carbon Dioxide. The velocity and amount of sorption of carbon dioxide by the dehydrated silica gel have been measured. The results are given in Table 3.

Table 3. Sorption of CO₂ by Silica Gel.

Time in min.	Pressure of gas in mm.	Vol. of CO ₂ (N.T.P.) sorbed at 25°C. by 1 gr. of gel in c.c.
0.5	754.7	4.66
1	754.7	5.03
2	754.7	5.38
5	754.7	5.56
10	754.7	5.66
60	754.4	5.82
255	753.7	5.93
1380	753.6	6.08
2995	756.5	6.16
11490	759.4	6.27
34550	761.6	6.34
82050	761.7	6.40

Sorption of Ethylene. The results of measurement on ethylene by dehydrated gel are shown in Table 4.

Table 4. Sorption of C₂H₄ by Silica Gel.

Time in min.	Pressure of gas in mm.	Vol. of C ₂ H ₄ (N.T.P.) sorbed at 25°C. by 1 gr. of gel in c.c.
0.5	758.8	3.81
1	758.8	3.98
2	758.8	4.12
4	758.7	4.20
9	758.6	4.22
40	758.4	4.26
305	757.9	4.29
1490	760.4	4.34
3080	764.4	4.37
17580	760.0	4.43
31930	760.0	4.47
60750	760.0	4.48
99600	760.0	4.50

The theoretical discussion on the velocity of sorption will be done in the next communication.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

A NEW METHOD OF ESTIMATING CATAPHORETIC VELOCITY IN A CONCENTRATED SUSPENSION.

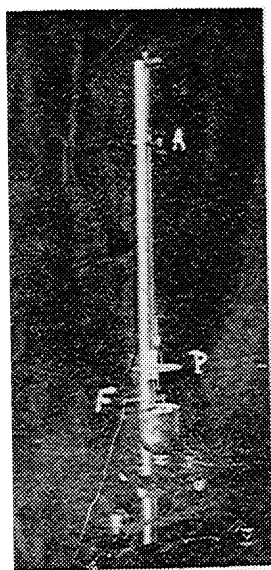
By Sakuji KOMAGATA.

Received February 25th, 1932. Published May 28th, 1932.

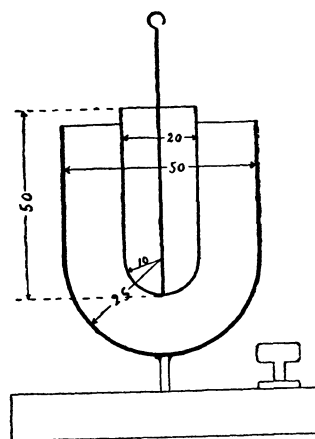
Among the methods hitherto known, the U-tube method is only applicable for the measurement of cataphoretic velocity in a concentrated suspension. The author has recently devised a new method which may be called the *weight method*. In the present paper, the general outline of this new method is briefly described.

Apparatus. When a suspension is placed under the influence of an electric field, the cataphoresis occurs and causes the particles in the suspension to gather on the surface of the electrode. It is the necessary condition for the applicability of the weight method to be the sample undisperse and so concentrated that the weight increase of deposition is measurable.

The present apparatus used is as shown in Fig. 1. The upper electrode used as collecting electrode is hung at the end of the spring and the other



(a)



(b) Electrode-configuration
(scale in mm.)

Fig. 1.

is fixed against it. When the electromotive force is applied between them, the cataphoresis occurs which would cause the suspended system to descend gradually. But at this moment, the system is adjusted so as to keep itself in the original position by the mechanism of rack and pinion (A) attached to the apparatus. The displacement of rack on this adjustment is read by the scale, indicating the quantity relating to the increased weight of deposition. To avoid to flow current in the spring, the ebonite piece is connected between the electrode and the spring, which makes inconvenient to feed current to the electrode. But, in the present case, the feeding is made by mean of the 2 amp. fuse connected directly with the electrode and the calibration of spring is obtained under such condition. The connection diagram is as shown in Fig. 2.

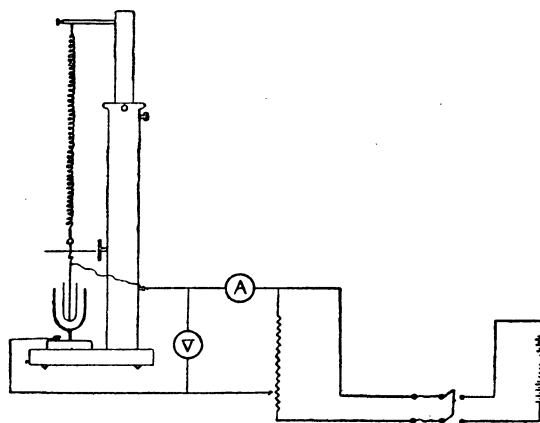


Fig. 2.

Principle. Let W (gr.) be the increase of reading of spring balance i. e. the weight of deposition in suspension and W_a (gr.) the weight of deposition in air, then the difference between W_a and W is equal to the weight of suspension occupied by the deposition i. e. the buoyancy W_b .

$$W_b = W_a - W \dots\dots\dots (1)$$

And, let v (cm./sec.) be the rate of increase of deposition, d the specific density of suspension, A the effective area of electrode and t the time, then we have

$$v = \frac{1}{d} \frac{1}{A} \frac{dW_b}{dt} = \frac{1}{d} \frac{1}{A} \frac{d(W_a - W)}{dt} \dots\dots\dots (2)$$

But it occurs in general that the distribution of particles, accordingly, that of voltage change with the lapse of time. Furthermore, the part of voltage impressed for the deposition and the effects of electrolysis appear and increase seriously with time. Therefore, it is impossible to obtain the time-relation of equation (2) experimentally. To eliminate such difficulties, the limiting state at $t = 0$ must be considered as follows :

$$(v)_{t=0} = \frac{1}{d_0} \frac{1}{A} \left\{ \frac{d(W_a - W)}{dt} \right\}_{t=0} \dots\dots\dots (3)$$

where d_0 is the specific density of sample itself. As the distribution of voltage is uniform G at this very case, the velocity $(v)_{t=0}$ for unit voltage gradient is given by

$$v_0 = \frac{(v)_{t=0}}{G} = \frac{1}{d_0} \frac{1}{A} \frac{1}{G} \left\{ \frac{d(W_a - W)}{dt} \right\}_{t=0} \dots\dots\dots (4)$$

Now let P_0 (%) be initial weight percentage of particles in sample and P_0' be the limiting value of weight percentage of particles in deposition at $t = 0$, then we have

$$v_0 p_0' GA = u_0 p_0 GA$$

Therefore, cataphoretic velocity u_0 is given by

$$u_0 = \frac{p_0'}{p} v_0 = \frac{1}{d_0} \frac{1}{A} \frac{1}{G} \frac{p_0'}{p_0} \left\{ \frac{d(W_a - W)}{dt} \right\}_{t=0} \dots\dots\dots (5)$$

The factors given in above equation (5) can easily be determined by the use of the author's apparatus :—

(i) A : The KCl solution having known conductivity κ is put into the vessel and the resistance R is measured by the Kohlrausch Bridge. Then A , the effective area of electrode, is obtained by

$$A = \frac{l}{R\kappa} \dots\dots\dots (6)$$

where l is the distance between the electrodes.

(ii) G : The correction for the polarisation on the electrode, the voltage drop in the feeding wire and so on must be considered in this case. For

this purpose, the several measurements are carried out under the various impressed voltages. The relation between W and the applied voltages V ,

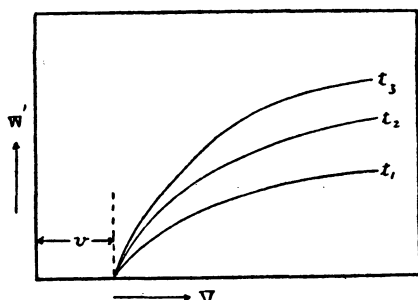


Fig. 3.

its parameter being time, is obtained such as shown in Fig. 3. The intersection of the group of curves and the abscissa gives the required correction by the following relation.

$$G = \frac{V-v}{l} \dots\dots\dots (7)$$

(iii) p_0' : p_0' is obtained by the extrapolation of $p'-t$ curve. (p' = weight percentage of particles in deposition)

(iv) $\left\{ \frac{d(W_a - W)}{dt} \right\}_{t=0}$: Drawing out carefully the suspended system into air, W_a is measured by the apparatus. $\{d(W_a - W)/dt\}_{t=0}$ is obtained by the tangent of $(W_a - W)-t$ curve at $t = 0$.

Experimental Results: 250 Gr. of clay is mixed with l liter of 1/250 N.—NaOH aqueous solution and the mixture is shaken for five hours and is left at one night long. The upper part of this mixture is taken out as sample. The experimental data are tabulated as follows:

(1) Ball clay:

Applied voltage		W' = reading of spring balance (cm.) W_a = weight of deposition in air (gr.) W_d = weight of deposition in dry state (gr.). $p' = (W_d/W_a) \times 100$ (%)							
		t	1 min.	2	3	4	5	W_a	W_d
(a)	6	W'							
		I	0.50 cm.	—	—	—	—	1.77	0.48
		II	0.50	1.00	—	—	—	2.90	0.85
		III	0.50	1.00	1.30	—	—	3.94	1.17
		V	0.50	0.90	1.25	1.50	1.75	5.25	1.68
		mean	0.50	1.00	1.28	1.50	1.75		32.06

(Concluded)

(b) 12	$\begin{matrix} t \\ W' \end{matrix}$	1 min.	2	3	4	5	W_a	W_d	p'
	I	0.80 cm.	—	—	—	—	3.07	0.94	30.62
	II	0.75	1.40	—	—	—	4.51	1.55	34.25
	III	0.75	1.40	2.00	—	—	6.33	2.30	36.33
	V	0.75	1.40	2.02	2.67	3.22	8.77	3.40	38.77
	mean	0.76	1.40	2.01	2.67	3.22			

(c) 18	$\begin{matrix} t \\ W' \end{matrix}$	1 min.	2	3	4	5	W_a	W_d	p'
	I	1.05 cm.	—	—	—	—	3.65	1.18	32.33
	II	1.07	2.05	—	—	—	5.95	2.18	36.72
	III	1.03	2.03	2.97	—	—	8.25	3.20	38.81
	V	1.05	2.07	3.03	4.02	4.90	13.42	5.80	43.22
	mean	1.05	2.05	3.00	4.02	4.90			

Then, we have

	V volt	G volt/cm.	$\left(\frac{d(W_a - W)}{dt}\right)_{t=0}$ gr./sec.		v_0 (cm./sec.) volt/cm.	p_0' %		u_0 (cm./sec.) volt/cm.
a	6	2.67	0.0167		16.3×10^{-5}	22.8		23.8×10^{-5}
b	12	6.67	0.0317	$A = 35.6$ cm.	12.3×10^{-5}	24.8	$p_0 = 12.87$	23.7×10^{-5}
c	18	10.67	0.0433	$d_0 = 1.076$	10.6×10^{-5}	26.8		22.1×10^{-5}
	$v = 2.0$			(mean)	12.7×10^{-5}		(mean)	24.8×10^{-5}

(2) China clay :

(a) 6	$\begin{matrix} t \\ W' \end{matrix}$	1 min.	2	3	4	5	W_a	W_d	p'
		0.35 cm.	—	—	—	—	1.90	0.70	31.69
	I	0.45	0.80	—	—	—	2.85	1.02	35.83
	II	0.35	0.70	1.05	—	—	4.00	1.45	38.32
	V	0.45	0.78	1.05	1.45	1.75	5.88	2.44	41.49
	mean	0.40	0.76	1.05	1.45	1.75			

W' = reading of spring balance (cm.)
 W_a = weight of deposition in air (gr.)
 W_d = weight of deposition in dry state (gr.)
 $p' = (W_d/W_a) \times 100$ (%)

(Concluded)

(b) 12	$\begin{matrix} t \\ W' \end{matrix}$	1 min.	2	3	4	5	W_a	W_d	p'
	I	0.70 cm.	—	—	—	—	3.05	1.17	38.36
	II	0.70	1.40	—	—	—	5.00	2.21	42.20
	III	0.60	1.35	1.87	—	—	6.61	2.95	44.63
	V	0.60	1.30	1.95	2.55	3.00	9.80	4.62	47.19
	mean	0.65	1.35	1.91	2.55	3.00			

(c) 18	$\begin{matrix} t \\ W' \end{matrix}$	1 min.	2	3	4	5	W_a	W_d	p'
	I	1.10 cm.	—	—	—	—	4.33	1.74	40.18
	II	1.10	2.20	—	—	—	7.42	3.27	44.02
	III	1.00	2.10	3.00	—	—	10.14	4.80	47.33
	V	1.00	2.00	3.10	4.10	5.05	14.87	7.49	50.38
	mean	1.05	2.10	3.05	4.10	5.05			

Then, we have

	V volt	G volt/cm.	$\left(\frac{d(W_a-W)}{dt}\right)_{t=0}$ gr./sec.		v_0 (cm./sec.) (volt/cm.)	p_0'		u_0 (cm./sec.) (volt/cm.)
a	6	2.27	0.0180	$A=35.6$ cm.	20.1×10^{-5}	23.0	$p_0=16.23$	28.4×10^{-5}
b	12	6.27	0.0350	$d_0=1.108$	14.1×10^{-5}	33.6		29.1×10^{-5}
c	18	10.27	0.0533		13.1×10^{-5}	35.6		28.8×10^{-5}
$v=2.6$				(mean)	15.6×10^{-5}		(mean)	28.7×10^{-5}

U-tube Method: For the purpose of comparison, the U-tube method is also carried out for the same samples. The apparatus used is as shown in Fig. 4. The method of measurement is, in almost all the parts, same as that of H.R. Kruyt and P. C. van der Willigen⁽¹⁾. The results obtained are given in the following table, which coincide well with those obtained by the weight method:—

	u_0
Ball clay	22.0×10^{-5} cm. / sec. / volt / cm.
China clay	28.0×10^{-5} „

(1) *Kolloid. Z.*, **44** (1928), 22.

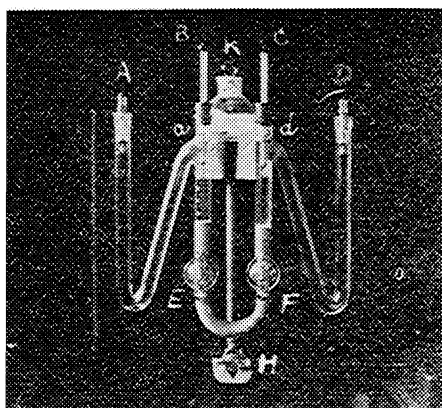


Fig. 4.

Lastly, the author expresses his hearty thanks to Mr. Iwasaka for his assistance in carrying out the experiments.

Summary: The results of the weight method coincide well with those of U-tube method. Although there are many points to be improved in the present apparatus, the author believes that the method is of some value, as it is, for the reason that there are few methods for the measurement of cataphoretic velocity in a heavily concentrated suspension. The author has designed the apparatus operating automatically under the same principle, results of which will be reported in a near future.

Electrotechnical Laboratory, Ministry of Communications,
Kōjimachi, Tokyo.

STUDIES ON REACTIONS BETWEEN GAS AND SOLID.
III. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT
OF PRESSURE OF NITROGEN ON THE
REACTION VELOCITY.

By Takeo AONO.

Received February 27th, 1932. Published May 28th, 1932.

From a kinetic study of the reaction $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$, G. Bredig⁽¹⁾ and his coworkers found that the azotation velocity of the carbide is proportional to the N_2 -pressure. But F. Foerster and H.

(1) Bredig, Fränkel and Wilk, *Z. Elektrochem.*, **13** (1907), 605.

Jacoby⁽¹⁾ stated from their experiments that „Dies zeigt, dass zwar ein Druckeinfluss bei der CaCN_2 -bildung vorhanden, dass er aber nur von geringer Bedeutung ist.“ As this problem is significant for the study of the chemistry of calcium cyanamide, the present experiment has been carried out to ascertain whether this proportional relation really or to what extent exists or not.

Experimental.

A nickel boat of 1 cm. wide and 5 cm. long, containing powders or grains of technical calcium carbide mixed with CaF_2 (1 and 5% in weight), was placed in a porcelain tube, one end of which being sealed. The other end of the tube was connected both with a nitrogen source and a Hg manometer and an air pump through a three way cock. The tube was very carefully tested whether it was perfectly gas-tight in heated state or not. After searching several kinds, the author obtained a proper material specially made by the S.C.P. Co. N_2 -gas which contained 0.24% of O_2 , was purified with heated Cu, conc. H_2SO_4 and sodalime, and then dried with CaCl_2 and P_2O_5 . After the carbide had been heated in vacuum up to a proper temperature until no gases were expelled from the carbide and the tube, the N_2 -gas was led into it for a few minutes. At the beginning of the azotation of carbide, the reaction velocity varies considerably from time to time even at a constant N_2 -pressure. After a certain time the change of reaction velocity becomes so slow as it may be regarded as constant in a short time interval. The measurement was executed at this stage in two ways.

The one way was as follows. Decreasing or increasing the total pressure (P) of the N_2 -gas in the reaction tube, the time (Δt) needed for each 8 mm. of the pressure decrease (ΔP) was measured with a stop watch. The slight change of the total volume due to the change of the manometer hight was also measured and the correction (F) for it was calculated as follows. If we denote by V the total volume of the gaseous space at the manometer reading of 760 mm., and by v the volume decrease due to the change of manometer hight, then we have $F_1 = V/(V-v_1)$, $F_2 = V/(V-v_2)$, etc. at the pressure P_1 , P_2 , etc. respectively. And

$$dt = \frac{\Delta t}{8} F.$$

(1) Foerster and Jacoby, *Z. Elektrochem.*, **12** (1907), 101.

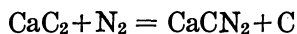
The pressure P was determined from the following equation

$$P = B - \left[2(h-a) + \frac{\Delta P}{2} + (c-c') \right],$$

where B : the barometer reading of the atmosphere; a : mean height of the manometer reading; c, c' : heights of the menisci; h : reading of the circular edge of the meniscus of the higher column.

The other way was to measure the rate of decrease of the N_2 -pressure as G. Bredig had done; but as this method takes longer time to accomplish one set of measurement, and from fear that the reactivity of the material might change during the course of measurement, the former way was preferred.

Experimental Results. At a constant temperature the velocity of the reaction



will be a function of both the pressure of N_2 and the reactive solid material. In a proper condition and in a small time interval the reactivity of the carbide may be regarded as constant, and the reaction velocity will change solely with the N_2 -pressure. If there holds the proportional law between them, then we must have the following relation at constant N_2 -volume:

$$-\frac{dP}{dt} = kP \quad \dots\dots\dots (1)$$

where $-dP$ means the decrease of N_2 -pressure during the small time dt , and k the velocity constant. From equation (1) we have

$$k_2 = -\frac{dP}{P dt} \quad \dots\dots\dots (2),$$

or

$$k_3 = \frac{2.303}{t_2 - t_1} \log \frac{P_1}{P_2} \quad \dots\dots\dots (3).$$

Some of the results of two sets of the measurements are given in Tables 1, 2, 3 and 4. Each in Tables 1 and 2, 3 and 4 belongs to the same series respectively.

Table 1.

Method 1. Powdered carbide ($\text{CaC}_2 = 67.4\%$ and $\text{CaF}_2 = 1.2\%$)

No.	Temp. °C.	P_{N_2} mm.	Δt . sec.	F	$-P \frac{\Delta t}{\Delta P}$	$k_2 \times 10^3$
1	786	55.9	376	1.071	2815	0.355
2	787	271.3	95.5	1.048	3375	0.296
3	789	441.1	78.8	1.031	4476	0.233
4	790	561.5	67.8	1.019	4848	0.222
5	790	651.7	64.0	1.010	5260	0.190
6	791	753.5	60.0	1.000	5650	0.170
15	866	228.7	100	1.053	3010	0.332
16	867	395.7	61.6	1.035	3148	0.318
17	868	601.9	47	1.015	3590	0.278
18	870	749.5	40	1.001	3752	0.266
19	870	741.3	42	1.002	3904	0.256
20	870	540.1	53.6	1.021	3766	0.266
21	870	335.9	81	1.042	3545	0.282
22	870	97.3	240	1.068	3118	0.327
23	945	250.9	16.0	1.051	528	1.89
24	945	451.1	10.8	1.030	626	1.59
25	945	574.7	8.2	1.018	600	1.66
26	945	554.3	7.8	1.019	551	1.81
27	945	534.1	9.2	1.022	628	1.59
28	945	635.5	7.4	1.012	596	1.68
29	945	615.1	7.6	1.014	592	1.69
30	946	720.7	6.6	1.003	596	1.68
31	946	655.7	6.0	1.009	496	2.01
32	947	631.3	7.4	1.012	592	1.69
33	948	710.5	7.1	1.009	636	1.57
34	948	755.5	6.8	1.000	641	1.56
96	1007	749.6	6.2	1.001	581	1.72
97	1007	492.3	7.6	1.026	479	2.08
98	1007	526.3	8.6	1.023	578	1.73
99	1008	319.7	13.8	1.043	575	1.74
100	1008	153.9	27.8	1.061	568	1.76

Table 2.
Method 2. (Continued to Table 1.)

No.	Temp. °C.	<i>P</i> mm.	$t_2 - t_1$ sec.	$k_3 \times 10^3$
35	950°	759.7	61.9	1.36
38	"	698.3	67.6	1.35
41	"	637.5	75.0	1.35
44	"	576.0	83.9	1.31
47	"	515.9	94.2	1.33
50	"	455.1	107.5	1.33
53	"	394.5	81.5	1.32
55	"	354.1	91.4	1.32
57	"	313.7	102.8	1.35
59	"	273.1	56.0	1.37
60	"	252.9		

Table 3.
Method 1. Grainy carbide⁽¹⁾ (61.9% CaC₂, 5% CaF₂—powder).

No.	Temp. °C.	<i>P</i> mm.	Δt sec.	<i>F</i>	$-P \frac{\Delta t}{\Delta P}$	$k_2 \times 10^3$
11	1028	528.6	50	1.022	338	2.96
12	1029	285.0	6.3	1.047	235	4.25
13	1030	709.2	4.6	1.004	410	2.44
14	1030	648.2	5.1	1.010	417	2.40

- (1) This carbide was specially prepared for this research by Mr. Hibi's process. The grain had a size of 1~3 mm. in diameter and was porous, the surface being covered with a thin film of carbon.

Table 4.
Method 2. (Continued to Table 3.)

No.	Temp. °C.	P mm.	t . sec.	$t_2 - t_1$ sec.	$k_3 \times 10^3$
26	1028	391.0	0	47	1.12
27	„	370.8	47	54	0.93
28	„	352.6	101	56	1.05
29	„	332.4	157	63	1.00
30	„	312.2	220	63	1.06
31	„	292.0	283		

Now, looking at the Tables 2 and 4, we find that the velocity constants k_3 calculated from equation (3) are gradually decreasing at first and then slightly increasing with P or time, while most of k_2 from the equation (2) increase with decreasing pressures. The decrease or constancy of k_3 could be attributed to the decrease of active mass with time, because it takes much time to accomplish one set of measurement. The increase of k_2 could not be attributed to any error involved in the operation such as inconstancy of temperature, change of reacting mass, etc. This can be recognized when the figures are carefully observed. It was assumed that

$$\frac{\Delta t}{\Delta P} = \frac{dt}{dP} = 1 \left/ \frac{dP}{dt} \right.,$$

and ΔP was taken as 8 mm., while the arithmetical mean pressure was taken as the corresponding P . Tracing $\left(\frac{-\Delta t}{\Delta P} \sim P \right)$ curves we see that in the region of these experiments

$$\left| \frac{dP}{P dt} \right| \geq \left| \frac{\Delta P}{P \Delta t} \right| \dots\dots\dots (4),$$

and this difference must, if any, increase with decreasing P . Hence the velocity constants found by this experiment would have to become rather smaller as P diminishes, which contradicts to the experiment. From

these reasons, the increase of k_2 with decreasing P could not be attributed to any error.⁽¹⁾

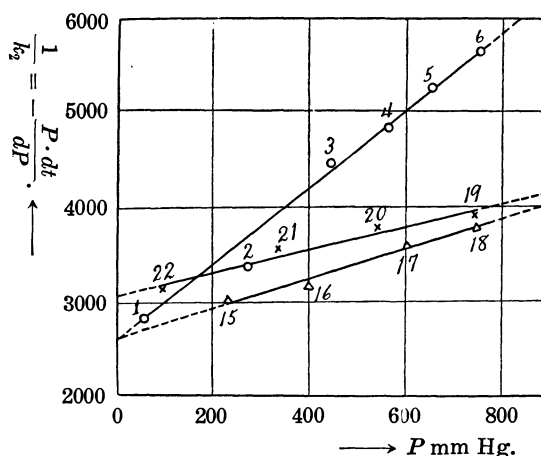


Fig. 1.

Tracing $\left(-P \frac{dt}{dP}\right) \sim P$ curves from these data we have, for example, Fig. 1 (from Table 1). The points lie almost on straight lines. Therefore we have

$$-P \cdot \frac{dt}{dP} = aP + b \quad \dots \dots \dots (5)$$

or

$$-\frac{dP}{dt} = \frac{P}{aP + b} = K \frac{P}{1 + \alpha P} \quad \dots \dots \dots (6)$$

It is important that a and α decrease with rising temperatures, as are seen in Table 5, which was calculated from the experimental values in Table 1.

Table 5.

Temp. °C.	From No.	for P in mm. Hg.				for P in atms.	
		a	b	K	α	K'	α'
790	1—6	4.07	2540	0.000394	0.00161	0.300	1.22
869	15—22	1.36	2840	0.000352	0.000479	0.268	0.364
946	23—34	0.125	530	0.00189	0.000236	1.44	0.179
1008	96—100	0.022	565	0.00177	0.000039	1.35	0.030

(1) When the data of Bredig's report (loc. cit.) are carefully observed, we can find that their k also increases with decreasing pressure.

Although the quantitative relation cannot be deduced directly from these data because the active surface and also the reactivity must change with proceeding of the reaction, we see that, the higher the temperature the greater is the effect of pressure-increase to the reaction velocity, though the effect of the pressure-increase becomes smaller at higher pressures.

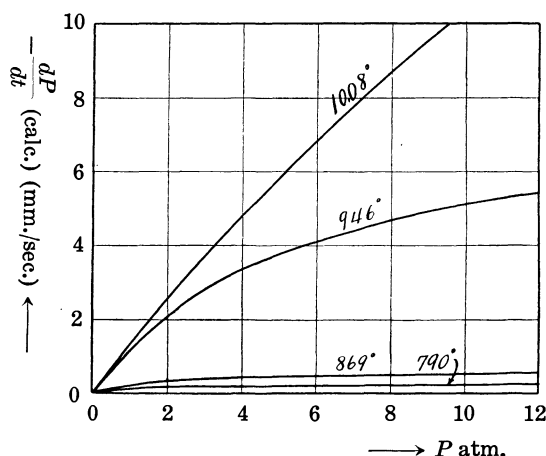


Fig. 2.—Relations btw. reaction velocity and nitrogen-pressure at various temperatures. (only qualitative.)

At lower pressures the reaction velocity is nearly proportional to the N_2 -pressure. From Table 5 we have Table 6 and Fig. 2. The numerical values cannot be compared with each other, because the reactivities of the carbide in each case are not equal, but we can see the tendency of the reaction velocity influenced by the pressure.

Table 6.

Relation between $-\frac{dP}{dt}$ and P (atm.) (calculated).

Temp. °C.	$-\frac{dP}{dt}$				
	$P = 1$ atm.	$P = 3$ atm.	$P = 5$ atm.	$P = 10$ atm.	$P = 20$ atm.
790	0.135	0.193	0.211	0.227	0.236
869	0.197	0.385	0.475	0.578	0.640
946	1.24	2.82	3.80	5.16	6.29
1008	1.31	3.72	5.87	10.38	16.88

The velocity of N_2 -absorption of carbide at constant temperature and pressure increases at first to a certain limit and then gradually decreases. The maximum velocity and its position is a function of temperature, the higher the temperature the greater is the maximum value and the position comes faster. These characteristics were studied by the author in many cases, which will be reported in the following papers in details but one of them will be cited here.

Powdered carbide ($CaC_2=72.97\%$), mixed with 10.0% of freshly ignited and dehydrated calcium chloride powder, was heated in vacuum up to $870^\circ C.$ and at this constant temperature nitrogen was led in. Keeping the pressure of nitrogen constant at 775 mm., the velocity of decrease in pressure per second was measured. After 20 minutes the pressure was varied and the reaction velocity or the rate of decreasing of the pressure was measured simultaneously with the corresponding pressure. The results are shown in Table 7 and Fig. 3-5.

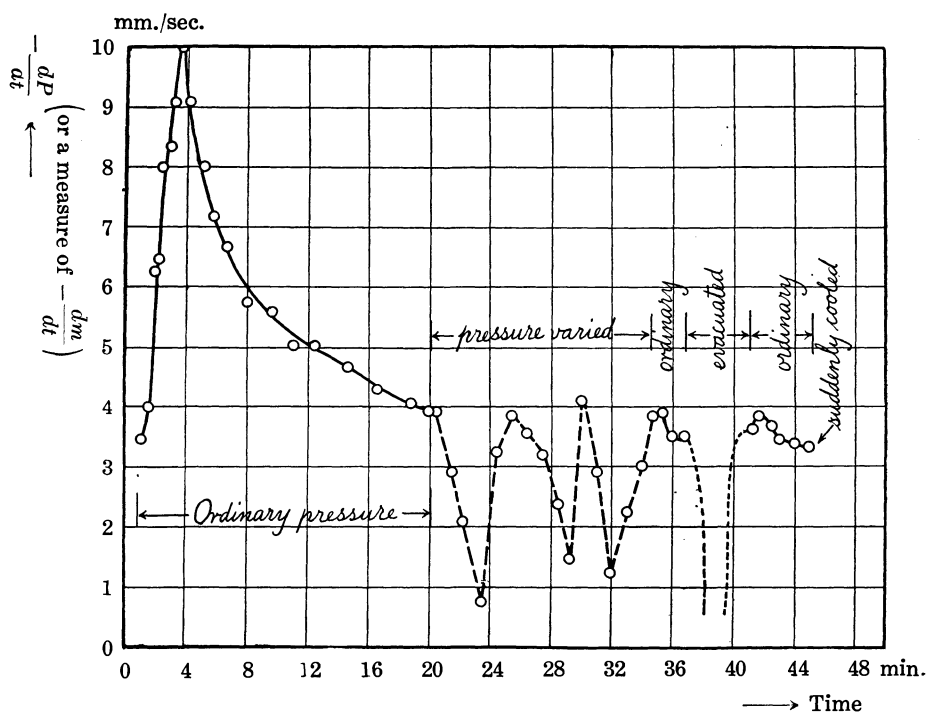


Fig. 3.—Velocity of azotation of powdered carbide with $CaCl_2$ (10%).

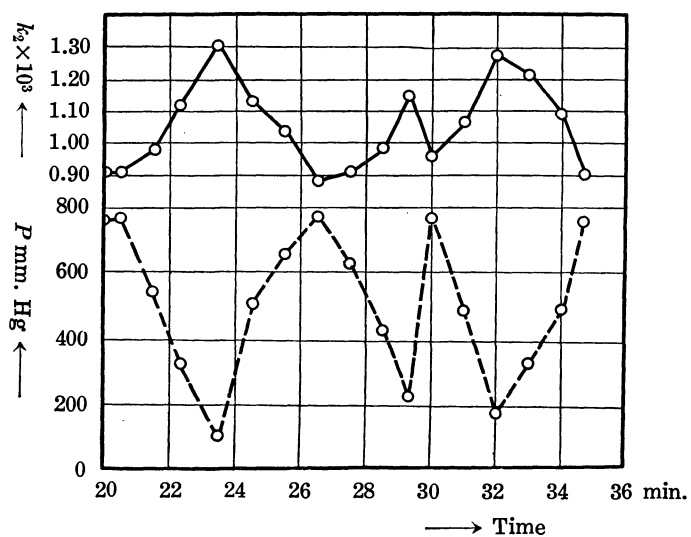


Fig. 4.—Relations btw. P and k_2 with proceeding time.

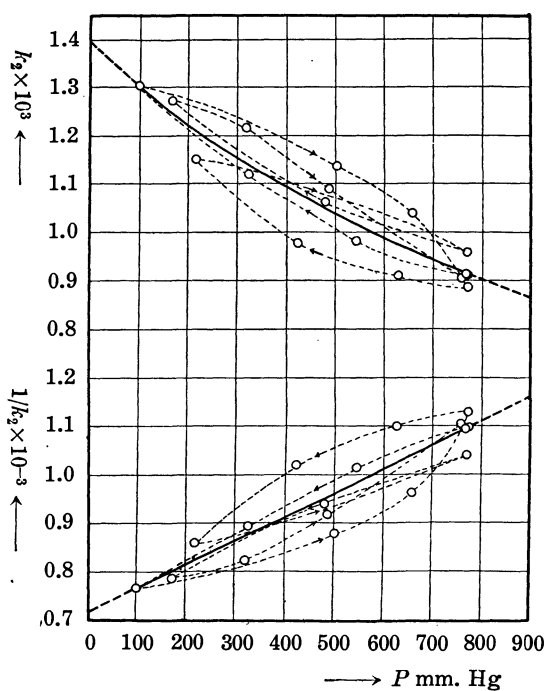


Fig. 5.—Change of k_2 with varying pressures.

Table 7. Calcium-carbide (72.97% CaC₂) + 10% CaCl₂.Furnace temp. = 870°C., $-\frac{dP}{dt} = \text{mm. } \alpha\text{-Br-naphthalene/sec.}$ $F = \text{correction factor.}$

Time min.	P _{N₂} mm. Hg.	$-\frac{dP}{dt}$ mm. Br-na./sec.	$-\frac{dt}{dP}$ sec./mm. Hg.	F	$\frac{1}{k_2} = -P \cdot \frac{dt}{dP} \cdot F$	$k_2 \times 10^3$
0	0→775	—				
1.0	775	3.45				
1.5	"	4.00				
2.0	"	6.25				
2.3	"	6.45				
2.5	"	8.00				
3.0	"	8.35				
3.3	"	9.10				
3.7	"	10.00				
4.3	"	9.10				
5.2	"	8.00				
5.8	"	7.15				
6.8	"	6.67				
8.2	"	5.72				
9.8	"	5.55				
11.2	"	5.00				
12.7	"	5.00				
14.8	"	4.65				
16.8	"	4.25				
19.0	"	4.00				
20.0	769	3.90	1.42	1.002	1095	0.914
20.5	773	3.90	1.42	1.000	1097	0.913
21.5	545	2.93	1.89	1.013	1016	0.985
22.3	325	2.07	2.67	1.027	892	1.121
23.5	99	0.75	7.42	1.042	766	1.305
24.5	503	3.22	1.72	1.016	879	1.138
25.5	659	3.82	1.45	1.007	963	1.039
26.5	773	3.79	1.46	1.000	1128	0.887
27.5	627	3.18	1.74	1.009	1100	0.910
28.5	423	2.34	2.36	1.021	1020	0.981
29.3	215	1.44	3.85	1.035	857	1.154
30.0	771	4.10	1.35	1.000	1041	0.961
31.0	481	2.88	1.92	1.017	939	1.065
32.0	169	1.24	4.47	1.038	785	1.275
33.0	319	2.21	2.50	1.028	821	1.218
34.0	487	2.99	1.85	1.017	917	1.091
34.7	759	3.82	1.45	1.005	1106	0.906
35.5	775	3.92	evacuated			
36.0	"	3.51				
36.3	"	3.51				
36.8	"	3.51				
41.3	775	3.64				
41.6	"	3.85				
42.5	"	3.70				
43.0	"	3.45				
44.0	"	3.39				
45.0	"	3.33				

It is interesting that when the pressure was changed suddenly, and $-\frac{dP}{dt}$ was measured without delay, then k_2 was greater than the value of k_2 corresponding to the equation at the elevation stage of the pressure and k_2 was smaller at the lowering stage of the pressure, or it has a hysteresis character. These interesting facts, together with other phenomena, have been treated by the author theoretically,⁽¹⁾ which will be reported in this bulletin in near future. These experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co., Ltd., Tokyo, before Sept. 10th (1930), and reported to the meeting of directors and engineers of the company on that day.

The author expresses his best thanks to Mr. K. Hibi, who gave him the opportunity of carrying out the experiments and allowed him to publish this report now. Mr. I. Kobayashi assisted him during the experiments.

Summary.

It has been experimentally determined that the velocity of reaction between nitrogen and calcium carbide at high temperatures is not directly proportional to the nitrogen-pressure, but there exists the following relation:

$$-\frac{dP}{dt} = K \frac{P}{1 + \alpha P},$$

where P denotes the pressure, K and α certain constants depending upon temperature and other conditions of the reaction.

It has also been found that the higher the temperature the greater is the effect of pressure-increase to the velocity of reaction, though the effect of the pressure-increase becomes smaller at higher pressures. At lower pressures the velocity of the reaction is nearly proportional to the pressure.

Research Laboratory of the Denki-Kagaku-Kogyo Co., Ltd.
(Electrochemical Manufacturing Co., Ltd.)
Yurakucho, Kojimachi-ku, Tokyo.

(1) Read before the meeting of the Chemical Society of Japan, Dec. 12th, 1931.

ELECTROLYTIC REDUCTION OF ALKYL-PHTHALIMIDES. IV. COMPLETE REDUCTION.

By Buhei SAKURAI.

Received February 27th, 1932. Published May 28th, 1932.

When acid imides of dicarboxylic acid, such as phthalimide is subjected to reduction, only one carbonyl group generally enters into reaction and is reduced to the corresponding secondary alcohol group or methylene group according to the conditions under which the reaction takes place, while another carbonyl group remains unaltered. Shortly before Goro Shima⁽¹⁾ succeeded in reducing the carbonyl group in many aldehydes and ketones completely to the corresponding hydrocarbon radical by passing an electric current of high density at the cathode composed of zinc amalgam. This suggests that a similar manner of electrolysis might, with a similar effect, be applied to the complete reduction of both carbonyl groups in the acid imide. With such an anticipation the writer undertook electrolytic reduction of phthalimide, methyl phthalimide, ethyl phthalimide and phenylphthalimide, and succeeded in fulfilling his expectation. Of the four imides above mentioned phenylphthalimide, however, could not be reduced to phenyl dihydroisindol, as it was hydrolysed into phthalic acid and aniline, before it underwent reduction.

The cathode of zinc amalgam was prepared in the following way:

Into a cylindrical cell having a diameter of 4.5 cm. mercury was introduced to the depth of about 1 cm., and after a conducting wire sealed up in a small glass tube was inserted into mercury a solution of zinc sulphate was poured into the cell as the catholyte. The cell was then placed in a glass cylinder which contained sulphuric acid of 6 normal as the anolyte. Now taking a lead plate as the anode a current of 2 amperes was passed between this and the mercury, which served as the cathode. The electrolysis was continued till the mercury completely solidified as zinc amalgam.

As the electrolyte, 12 normal sulphuric acid or hydrochloric acid was taken, and a current of high density, such as 30–60 amp./100 sq. cm. was passed at 80–90°C. using lead as the anode.

Experimental.

1. **Phthalimide.** The cathodic solution consisting of 120 c.c. of 12 normal sulphuric acid and 5 gr. of phthalimide was electrolysed with

(1) *Memo. Kyoto Imp. Univ.*, Series A, **12** (1929), 79.

the cathode of zinc amalgams (15 sq. cm.) by passing through it a current of 9.5 amperes. The current density at the cathode thus amounts to 60 am. / 100 sq. cm. The catholyte was kept stirred while electrolysed. Though after the lapse of 3.5 hours, the phthalimide in suspension had completely disappeared, electrolysis was continued as long again to ensure reduction. The temperature of the bath at the end of electrolysis rose to 90°C. On cooling with cold water the catholyte was made alkaline with caustic soda, when a brown oil separated out floating in the surface of the solution. It was extracted with ether and purified, and 3 gr. of an oil boiling at 213°C. were obtained. The material yield is thus 80% of the theoretical. It behaves as a base and easily changes into phthalimide when oxidized with potassium permanganate. On analysing it as its platinum double chloride (M.P. 252°C.) following result was obtained:

0.0619 Gr. of the double chloride gave on ignition 0.0184 gr. of Pt. Pt. = 29.73 %.
Calc. for $C_{16}H_{20}N_2PtCl_6$: Pt = 30.12 %.

These results in all respects precisely agree with pure chemically prepared dihydroisoindol.⁽¹⁾ So there is no doubt that both carbonyl groups were thus completely reduced into the methylene group.

By adding alcohol to the catholyte so as completely to dissolve all phthalimide, the reduction may be made to take place more smoothly and to finish in nearly 3.5 hours. Hydrochloric acid of similar normality may well be substituted for sulphuric acid in the electrolyte, but its use in such an experiment to be worked at high temperature is, of course, inconvenient in every respect.

2. Methyl Phthalimide. The conditions used for complete reduction of methyl phthalimide were as follows:

Cathode: zinc amalgam; Cathode solution: 120 cc. of 12 N. H_2SO_4 +5 gr. of the imide; Anode: lead; Anode solution: 12 N. H_2SO_4 ;
Current density: 60 amp./100 sq. cm.; Temperature: 85°C.; Time: 5 Hours.

After about an hour's electrolysis, the methyl phthalimide in the catholyte, which was always kept agitated, completely disappeared. The treatment of the electrolyte after the electrolysis was made in an analogous way as in the previous case, and about 3.2 gr. of an oil were isolated. The yield is calculated to be 80%. On keeping long in a cool place the oil was found partly crystallized into tabular crystals, the melting point of which was roughly determined to lie near 85°C. The melting point

(1) Gabril and Newmann, *Ber.*, **26** (1893), 526. Gabril and Pinkus, *Ber.*, **26** (1893), 2213. Fränkel, *Ber.*, **33** (1900), 2808. Brown, *Ber.*, **43** (1910), 1353.

of its platinum double chloride was determined as 199–200°C., and the result of the analysis was as follows:

0.0484 Gr. of the double chloride gave on ignition 0.0140 gr. of Pt; Pt = 28.91 %.
Calc. for $C_{18}H_{24}N_2PtCl_6$: Pt = 28.87 %.

These agree well with the methyl dihydroisoindol found by Fränkel.⁽¹⁾ The reduced product, thus identified as methyl dihydroisoindol was also observed to change back to methyl phthalimide, when oxidized with potassium permanganate.

3. Ethyl Phthalimide. The reduction experiment of ethyl phthalimide was carried out under the following conditions:

Cathode: Zinc amalgam; Anode: lead; Catholyte: 80 c.c. of 12 N. H_2SO_4 + 40 c.c. of alcohol + 5 gr. of the imide; Anolyte: 12 N. H_2SO_4 ; Current density: 38 amp./100 sq. cm.; Temperature: 80°C; Time: 7 hours.

The catholyte after electrolysis was coloured dark at high temperature; but become colourless when cooled. It was neutralized with caustic soda and a dark brown oil thus separated was purified after being extracted with ether. The yied was 2.5 gr., corresponding to 60% of the theoretical. It was analysed as its platinum double chloride (M.P. 192°C.) with the following result:

0.0475 Gr. of the double salt gave on ignition 0.0131 gr. of Pt. Pt = 27.69 %.
Calc. for $C_{20}H_{23}N_2PtCl_6$: 27.71 %.

The oil thus identified as ethyl dihydroisoindol⁽²⁾ was also confirmed to be oxidizable to ethyl phthalimide.

4. Phenyl Phthalimide and Ammonium Phthalate. Phenyl phthalimide and ammonium phthalate were subjected to the complete reduction in a manner analogous to that employed in the previous case, taking a saturated solution of ammonium carbonate as the anolyte. In neither case, however, could completely reduced products be obtained. Phenyl phthalimide was observed to change into phthalic acid and aniline, while ammonium phthalate partly changed to phthalide, but not to phthalane.

The writer wishes, in this opportunity warmly to thank Professor Motooki Matsui of Kyoto Imperial University, under whose kind suggestion this work was carried out.

February 20th, 1932.

Institute of Chemistry, Osaka Women's College.

Sumiyoshi, Osaka.

(1) *Ber.*, **33** (1900), 2815.

(2) Scholz, *Ber.*, **31** (1898), 1706.

GALVANISCHE ABSCHIEDUNG VON LEGIERUNGEN AUS METALLCYANIDEN IN CYANIDLÖSUNG.

Von Kosaku MASAKI.

Eingegangen am 8. März 1932. Ausgegeben am 28. Mai 1932.

Im Verlauf einer Arbeit über komplexe Cyanradikale von Metallen hatte der Verfasser Gelegenheit einige Studien über die galvanische Abscheidung verschiedener Legierungen aus Metallcyaniden in Cyanidlösung zu machen. Messing, Silber-Cadmium-, Kupfer-Cadmium-, Kupfer-Silber- und Kupfer-Nickel-Legierungen sind bereits von einer Anzahl Forscher untersucht worden. So hat Morgan⁽¹⁾ in seiner Arbeit über die Abscheidung von Messing aus einer Lösung der komplexen Cyanide von Kupfer und Zink festgestellt, dass komplexe Ionen von Kupfer und Zink anwesend sein müssen und dass die Konzentration der Kupferionen möglichst klein gehalten werden soll, damit eine gute Abscheidung erfolgt. Einige andere Forscher⁽²⁾ haben auch die Abscheidung von Messing aus Cyanidlösungen bearbeitet und den Einfluss der Temperatur und des Verhältnisses Kupfer-Zink studiert.

Aten und Putten⁽³⁾ haben eine Arbeit über Elektroplattierung mit Silber-Cadmiumlegierungen in einem Bade der Metallcyanide in Cyanid veröffentlicht und mitgeteilt, dass Cadmiumgehalt im Niederschlag mit steigender Stromdichte wächst. G. Tammann⁽⁴⁾ hat die Abscheidung einer Kupfer-Cadmium-Legierung aus der Lösung der Sulfate, Field⁽⁵⁾ die Abscheidung einer Kupfer-Silberlegierung aus Cyanidlösungen studiert. Proctor,⁽⁶⁾ Hineline und Cooley,⁽⁷⁾ sowie Stont, Burch und Langsdorf⁽⁸⁾ haben die Niederschlagung von Legierungen des Kupfers mit Nickel aus den komplexen Cyaniden untersucht.

Aber keiner der Forscher hat Angaben gemacht über die Potentiale zwischen Metall und Metallsalzlösung, obwohl es doch für die Ermittlung der jeweils günstigsten Arbeitsbedingungen bei der Abscheidung der

(1) *J. Am. Chem. Soc.*, **22** (1900), 93.

(2) Spitzer, *Z. Elektrochem.*, **11** (1905), 172; Field, *Trans. Faraday Soc.*, **9** (1909), 172; Bennett und Davison, *Trans. Am. Elektrochem. Soc.*, **25** (1914), 347; Honig, *Z. Elektrochem.*, **22** (1916), 286; Ferguson und Sturdevant, *Trans. Am. Electrochem. Soc.*, **38** (1920), 167.

(3) *Rec. Trav. Chem.*, **44** (1925), 861.

(4) *Z. anorg. Chem.*, **107** (1919), 1.

(5) *Z. Elektrochem.*, **17** (1910), 61.

(6) *Trans. Am. Electrochem. Soc.*, **23** (1913), 277.

(7) *Ibid*, **48** (1925), 61.

(8) *Ibid*, **57** (1930), 113.

Legierungen von grossem Wert wäre Genaueres über die auftretenden Spannungsdifferenzen aussagen zu können. Daher sollen in dieser Untersuchung stets zuerst die Potentiale Metall-Metallcyanid gemessen und dann auf Grund dieser Messungen die Abscheidungsbedingungen verschiedener Legierungen aus den komplexen Cyanidlösungen studiert werden.

Experimenteller Teil.

Herstellung der Metallcyanide. Die Sulfate von Kobalt, Cadmium, Kupfer, Nickel und Zink, sowie Silbernitrat wurden durch Umkristallisation gereinigt.

1) Cadmiumcyanid:⁽¹⁾ Kleine, gelbliche, rhombisch-prismatische Kristalle von Cadmiumcyanid wurden erhalten durch Zugabe einer Natriumcyanidlösung zu überschüssiger Cadmiumsulfatlösung.

2) Kobaltocyanid: Ein schwach rosa gefärbter Niederschlag von Kobaltocyanid wurde hergestellt durch Zusatz von Natriumcyanid zu Kobaltosulfat und durch Waschen mit Leitfähigkeitswasser gereinigt.

3) Kuprocyanid: Ein dicker weisser Niederschlag von Kuprocyanid liess sich erzielen durch Hinzufügung einer Natriumcyanidlösung zu Kupfersulfatlösung, die mit Schwefeldioxyd gesättigt worden war. Auch dieses Produkt wurde mit Leitfähigkeitswasser gereinigt.

4) Nickelcyanid⁽²⁾: Nickelcyanid wurde als apfelgrüne gelatinöse Fällung erhalten durch Mischung einer Natriumcyanidlösung mit überschüssigem Nickelsulfat.

5) Silbercyanid: Silbercyanid fiel als weisser, käsiger Niederschlag aus beim Versetzen einer Silbernitratlösung mit Natriumcyanid. Die Fällung wurde im Dunkelraum ausgeführt.

6) Zinkcyanid⁽³⁾: Eine weisse amorphe Fällung von anhydriischem Zinkcyanid wurde bereitet, indem Natriumcyanidlösung in Zinksulfatlösung gegeben wurde.

7) Mercuricyanid: Das in dieser Untersuchung verwandte Mercuricyanid war ein Kahlbaumsches Präparat.

Untersuchung der Materialien und Produkte. Die Konzentration der Natriumcyanidlösung wurde durch Titration mit Silbernitrat bestimmt, wobei zur leichteren Erkennung des Endpunktes Kaliumjodid als Indikator verwendet wurde. Die Analyse der Legierungen wurde so durchgeführt, dass nach der Auflösung in Salpetersäure das Silber mit

(1) K. Masaki, dieses Bulletin, 6 (1931), 60.

(2) K. Masaki, l. c., 233.

(3) K. Masaki, dieses Bulletin, 6 (1931), 89.

Kaliumchlorid als Chlorsilber, das Nickel in den Nickellegierungen mit einer 1%-igen alkoholischen Lösung von Dimethylglyoxim bestimmt wurde; andere Legierungen wurden auch durch Elektro-Analyse bestimmt.

Die Messungen der elektromotorischen Kräfte. Wir haben nun eine Reihe von Bestimmungen der Potentiale zwischen Metallelektroden und ihren Cyanidlösungen ausgeführt. Die für diese Messungen benutzten Lösungen wurden hergestellt durch Auflösen geeigneter Mengen der reinen Metallcyanide in jeweils 100 Teilen Natriumcyanidlösung wechselnder Konzentration; die Zelle war von der üblichen Form.

Die Messungen der elektromotorischen Kräfte wurden bei $25^\circ \pm 0.1^\circ$ gegen eine Normal-Kalomelektrode unter Anwendung einer gesättigten Kaliumchloridlösung als Zwischenelektrolyt gemacht. Folgende Ketten wurden gemessen:

- 1) $\text{Me} \mid \text{Me}(\text{CN})_2 \text{ oder } \text{MeCN}, x\text{n NaCN} \mid \text{KCl}(\text{ges.}) \mid \text{nKCl}, \text{HgCl} \mid \text{Hg}$
- 2) $\text{Me} \mid \text{MeSO}_4 \text{ oder } \text{Me}_2\text{SO}_4, x\text{n NaCN} \mid \text{KCl}(\text{ges.}) \mid \text{nKCl}, \text{HgCl} \mid \text{Hg}$
- 3) $\text{Me-Hg} \mid \text{Me}(\text{CN})_2 \text{ oder } \text{MeSO}_4, x\text{n NaCN} \mid \text{KCl}(\text{ges.}) \mid \text{nKCl}, \text{HgCl} \mid \text{Hg},$

wobei unter Me das in Frage kommende Metall zu verstehen ist; lediglich im Falle des Kobalts kam eine Amalgamelektrode zur Anwendung. Der Verfasser fand bei diesen Versuchen, dass die gemessenen Potentiale über einen Zeitraum von 30 Minuten und länger konstant blieben. Die mittlere Abweichung der erhaltenen EMK-Werte war in keinem Fall grösser als 0.0003 Volt. Die Ergebnisse sind in Tabellen 1, 2 und 3 zusammengestellt. Eine Umrechnung der Konzentrationen auf Aktivitäten wurde nicht vorgenommen und eine Berücksichtigung der Flüssigkeitspotentiale erübrigte sich auf Grund ihrer Elimination in der Messanordnung.

Tabelle 1.

Die elektromotorische Kraft von Metall in 0.05 molarer Lösung des Metallcyanids in Natriumcyanidlösungen wechselnder Konzentration gegen die Normal-Kalomelektrode.

NaCN xn	$\text{Cu}_2(\text{CN})_2$ (1)	$\text{Cd}(\text{CN})_2$ (2)	AgCN (3)	$\text{Ni}(\text{CN})_2$ (4)	$\text{Co}(\text{CN})_2$ (5)	$\text{Zn}(\text{CN})_2$ (6)
0.2786	0.8001	1.1380	0.6491	0.5768	0.6000	1.4664
0.5794	1.0862	1.1931	0.7550	0.6510	0.7308	1.5159
1.0099	1.3000	1.2106	0.7972	0.7002	0.7636	1.5417
1.4500	1.4726	1.2417	0.8273	0.7374	0.7823	1.5628
2.0015	1.5500	1.2603	0.8613	0.7715	0.8105	1.6000
3.1470	1.6233	1.2713	0.9128	0.7822	0.8374	1.6332

Tabelle 2.

Die elektromotorische Kraft von Metall in 0.01 molarer Lösung des Metallcyanids in Natriumcyanidlösungen wechselnder Konzentration gegen die Normal-Kalomelektrode.

NaCN xn	Cu ₂ (CN) ₂ (7)	Hg(CN) ₂ (8)	AgCN (9)	Ni(CN) ₂ (10)	Co(CN) ₂ (11)	Zn(CN) ₂ (12)
0.1456	1.0359	0.6000	0.6993	0.6152	0.6993	1.4800
0.5699	1.1200	0.6732	0.7927	0.6624	0.7452	1.5282
0.9751	1.1710	0.6992	0.8348	0.6720	0.7520	1.5776
1.6716	1.3132	0.7214	0.8857	0.6997	0.7964	1.6099
3.4414	1.5489	0.7521	0.9285	0.7059	0.8195	1.6569

Tabelle 3.

Die elektromotorische Kraft von Metall in einer 0.01 molaren Lösung des Metallsulfats in Natriumcyanidlösungen wechselnder Konzentration gegen die Normal-Kalomelektrode.

NaCN xn	CdSO ₄ (13)	Ag ₂ SO ₄ (14)	NiSO ₄ (15)	CoSO ₄ (16)	ZnSO ₄ (17)
0.3261	1.1607	0.7318	0.7867	0.7100	1.5179
1.3550	1.2591	0.8490	0.8979	0.7615	1.5949
2.6151	1.3031	0.9176	0.9100	0.7850	1.6423
3.4889	1.3281	0.9344	0.9286	—	1.6440

Wie man sowohl aus den Tabellen, wie auch aus den Kurven ersehen kann, sind die Potentiale Zink-Zinkcyanid und Zink-Zinksulfat in 0.01 molarer Lösung annähernd gleich. Es zeigt sich auch, dass die Potentiale Silber-Silbercyanid und Zink-Zinkcyanid bei niedrigen Konzentrationen von Silbercyanid, bzw. Zinkcyanid ansteigen, während sie im Falle von Nickel-Nickelcyanid, Kupfer-Kuprocyanid und Kobaltamalgam-Kobaltcyanid bei niedrigen Konzentrationen der Metallcyanide fallen. Bei den genannten Kurven erhielten wir auch eine Anzahl Schnittpunkte. Betrachten wir für diese Fälle die Nernstsche Formel

$$E = \frac{RT}{nF} \ln \frac{P}{P'}.$$

E ist hier das Gleichgewichtspotential, das überschritten werden muss, damit Metallionen sich aus der Lösung abscheiden können, P

ist der elektrolytische Lösungsdruck und n die Wertigkeit des Metalls, P' der osmotische Druck der Metallionen.

Nehmen wir jetzt den Schnittpunkt 1 in dem Kurvendiagramm. In diesem Punkte 1 muss E_{Cu} gleich E_{Cd} sein. Nach der Nernstschen Formel ergibt sich:

$$E_{Cu} = \frac{RT}{n_{Cu} F} \ln \frac{P_{Cu}}{P'_{Cu}} \dots\dots\dots (1)$$

$$E_{Cd} = \frac{RT}{n_{Cd} F} \ln \frac{P_{Cd}}{P'_{Cd}} \dots\dots\dots (2)$$

$$\text{Nun ist } E_{Cu} = E_{Cd} \text{ oder } \frac{RT}{F} \ln \frac{P_{Cu}}{P'_{Cu}} = \frac{RT}{2F} \ln \frac{P_{Cd}}{P'_{Cd}} \dots\dots\dots (3)$$

Wir können also voraussagen, dass sich unter den im Schnittpunkte der Kurven obwaltenden Bedingungen Legierungen abscheiden müssen. Die für die Elektrolyse notwendige Natriumcyanid-Konzentration ergibt sich aus den besagten Kurvenpunkten.

Abscheidung von Legierungen. Aus den obigen Versuchen ergaben sich folgende Zusammensetzungen für die Lösungen zur Abscheidung von Legierungen aus cyanidischem Bade. Die Versuchsergebnisse sind hier zusammengestellt.

(1) Kupfer-Cadmium-Legierungen.

Bez. der Lösung	Reagens	Mole pro Liter	Gramm pro Liter
A-Lösung	3CdSO ₄ ·8H ₂ O	0.01	7.6955
	Cu ₂ (CN) ₂	0.01	1.7916
	NaCN	1.33	65.1833
B-Lösung	Cd(CN) ₂	0.05	8.2215
	Cu ₂ (CN) ₂	0.01	1.7916
	NaCN	1.15	56.3615
C-Lösung	Cd(CN) ₂	0.05	8.2215
	Cu ₂ (CN) ₂	0.05	8.9580
	NaCN	0.72	35.2872

(2) Kupfer-Nickel-Legierungen.

Bez. der Lösung	Reagens	Mole pro Liter	Gramm pro Liter
D-Lösung	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	0.01	2.8087
	$\text{Cu}_2(\text{CN})_2$	0.05	8.9580
	NaCN	0.25	12.2525

(3) Silber-Nickel-Legierungen.

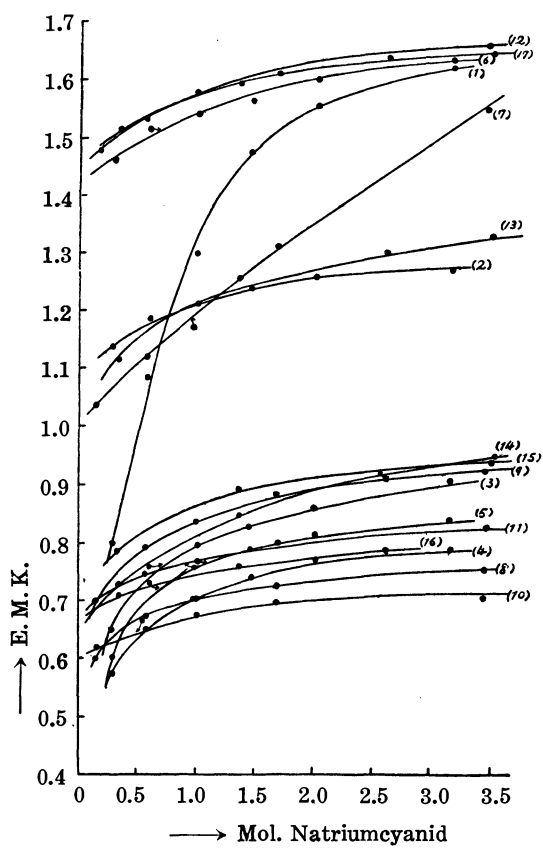
Bez. der Lösung	Reagens	Mole pro Liter	Gramm pro Liter
E-Lösung	AgCN	0.05	6.6945
	$\text{Ni}(\text{CN})_2$	0.01	1.1077
	NaCN	0.24	11.7624
F-Lösung	Ag_2SO_4	0.01	3.1182
	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	0.01	2.8087
	NaCN	3.25	159.2825

(4) Silber-Kobalt-Legierungen.

Bez. der Lösung	Reagens	Mole pro Liter	Gramm pro Liter
G-Lösung	AgCN	0.05	6.6945
	$\text{Co}(\text{CN})_2$	0.01	1.1099
	NaCN	0.51	24.9951
H-Lösung	Ag_2SO_4	0.01	3.1182
	$\text{Co}(\text{CN})_2$	0.01	1.1099
	NaCN	0.25	12.2525
I-Lösung	AgCN	0.01	1.3389
	$\text{Co}(\text{CN})_2$	0.01	1.1099
	NaCN	0.15	7.3515
J-Lösung	AgCN	0.05	6.6945
	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	0.01	2.8112
	NaCN	0.50	24.5050

(5) Nickel-Kobalt-Legierungen.

Bez. der Lösung	Reagens	Mole pro Liter	Gramm pro Liter
K-Lösung	Co(CN)_2	0.05	5.5495
	Ni(CN)_2	0.01	1.1077
	NaCN	0.35	17.1535
L-Lösung	Co(CN)_2	0.05	5.5495
	Ni(CN)_2	0.05	5.5385
	NaCN	0.22	10.7822



(1) **Galvanische Abscheidung von Silber- und Kobaltlegierungen.** Die Konzentrationen des Silber-, Kobalt- und Natriumcyanids sind bereits festgelegt worden. Die verwendete Badlösung war eine B-Lösung, in diesem Falle von zitronengelber Farbe, als Anoden dienten zwei Silberplatten von der Grösse $3 \times 5 \text{ cm.}^2$ und als Kathode eine Kupferplatte gleicher Grösse. Die Flüssigkeit wurde nicht gerührt. Die Elektrolyse wurde bei Zimmertemperatur durchgeführt (etwa 18°C.) und das Volumen der Flüssigkeit betrug 500 ccm., während ihre Schichthöhe 7 cm. war. Die Elektroden hatten einen Abstand von 4.5 cm.

Vor der Elektroplattierung mit Silber-Kobalt wurden die Kathoden einer gründlichen Reinigung unterworfen, indem sie in siedendheisser alkalischer Reinigungslösung elektrolytisch gesäubert und mit Wasser gut gespült wurden. Die Kathoden wurden dann in das Silber-Kobalt-Bad eingesetzt und der Strom eingeschaltet. Mit diesen Lösungen wurden die in Tabelle 4 aufgeführten Ergebnisse erhalten.

Tabelle 4.

Plattennummer	Zeit in Minuten	Stromdichte Amp./cm ² .	Kathodenpotential	Zellenspannung	Abgesch. Metall (gr.)	Ag/Co	Bemerkungen
11	30	0.0073	0.8311	1.30	0.2070	4	Grauweiße Farbe, feines Korn
12	30	0.0066	0.8237	1.25	0.1398	2.7	Gleiche, Farbe, feines Korn
13	30	0.0047	0.8234	1.20	0.1320	8.1	Hochglänzend
14	30	0.0030	0.8232	1.00	0.0942	3.6	Hochglänzend

Einfluss der Temperatur. Die Daten in Tabelle 5 zeigen den Einfluss der Temperatur auf das Verhältnis der Metalle im elektrolytischen Niederschlag, erhalten aus Bädern gleicher Zusammensetzung. Man sieht deutlich, dass das Verhältnis des Kobalts zum Silber ansteigt mit steigender Temperatur.

Tabelle 5.

Plattennummer	Temp.	Zeit in Min.	Stromdichte Amp./cm ² .	Zellenspannung	Abgesch. Metall (gr.)	Ag/Co	Bemerkungen
51	25	30	0.0033	0.8	0.1410	4.4	Dunkelgelbe Farbe
52	35	30	0.0033	0.8	0.1521	3.9	Glänzendweiße Farbe
53	60	30	0.0033	0.8	0.1800	3.7	Gleiche Farbe

Wie man aus Tabelle 5 erschen kann, steigt das Gewicht des Niederschlags mit steigender Temperatur.

(2) **Galvanische Abscheidung von Silber - Nickel - Legierungen.** Konzentration und Zusammensetzung der Bäder sind bereits beschrieben worden. Die jeweiligen Bedingungen waren die gleichen wie bei den Silber-Kobalt-Legierungen. Die Badlösung war von gelber Farbe. Bei diesen Versuchen wurde der Einfluss der Temperatur nicht weiter verfolgt. Die Ergebnisse sind im folgenden zusammengestellt:

Tabelle 6.

Plattennummer	Zeit in Min.	Stromdichte Amp./cm. ²	Kath. Potential	Zellen-spannung	Abgesch. Metall (gr.)	Ag/Ni	Bemerkungen
10	30	0.0088	0.7421	2.5	0.3018	4.6	Grauweiße Farbe
7	30	0.0044	0.7405	1.4	0.1950	4.7	„
9	30	0.0038	0.7341	1.3	0.1632	5.8	„
6	30	0.0022	0.7312	0.6	0.1203	7.2	„

Aus Tabelle 6 und der Kurve erkennen wir, dass die abgeschiedene Menge der Legierungen steigt mit steigender Stromdichte, dass aber das Verhältnis Silber zu Nickel fällt. Bei den Platten 10 und 7 hatten wir ein sehr feines Korn an den Rändern und bei 9 und 6 war die Oberfläche sehr glatt.

(3) **Galvanische Abscheidung von Kupfer- und Nickel-Legierungen.** Stont, Burch und Langsdorf⁽¹⁾ haben die elektrolytische Abscheidung von Kupfer- und Nickel-Legierungen unter verschiedenen Bedingungen untersucht, dabei den Einfluss der Badzusammensetzung und der Stromdichte studiert und sind auf Grund ihrer Resultate zu folgenden Schlüssen gekommen: (1) Man darf annehmen, dass die Legierungen von Nickel und Kupfer aus Lösungen erzielt werden, die Mischungen ihrer Kaliumcyanidkomplexe enthalten. (2) Die prozentuale Zusammensetzung der niedergeschlagenen Legierungen hängt von dem Metallverhältnis im Bade, von der kathodischen Stromdichte und von der Temperatur ab. (3) Erhöhung des Kupfergehalts im Bade erhöht den Kupfergehalt im Niederschlage, aber in einem viel geringeren Ausmasse, als aus dem Kupfergehalt des Elektrolyten geschlossen werden könnte. (4) Das Verhältnis Kupfer zu Nickel auf der Platte steigt

(1). Loc. cit.

linear mit der Temperatur. (5) Niedrige kathodische Stromdichte begünstigt die Bildung von Niederschlägen mit hohem Kupfergehalt. (6) Bäder von niedrigem Gehalt an freiem Cyanid sollten verwendet werden zur Erzielung möglichst hoher Niederschlagsmengen.

In unser Untersuchung wurden Konzentration und Zusammensetzung der Badlösung aus den bereits beschriebenen Kurven erhalten und die anderen Bedingungen in der gleichen Weise gewählt wie im vorhergehenden Fall. Die Farbe des Elektrolyten war diesmal von einer gelblichen Farbe. Als Anoden wurden zwei Nickelplatten verwendet. Die Legierungen liessen sich nicht unterhalb einer Stromdichte von 0.0080 Amp./cm.² erzielen. Die Resultate sind im folgenden zusammengestellt.

Tabelle 7.

Plattennummer	Zeit in Min.	Stromdichte Amp./cm. ²	Kath. Potential	Zellenspannung	Abgesch. Metall (gr.)	Cu/Ni	Bemerkungen
107	30	0.0458	0.8492	20	0.0736	8.3	Rötlichweisse Farbe
106	30	0.0295	0.8256	17	0.0680	13.5	Gleiche Farbe
105	30	0.0250	0.8035	13	0.0560	17.9	„
104	30	0.0183	0.7466	7	0.0490	28.5	„
102	30	0.0081	0.7225	3.3	0.0428	Kein Ni	„

Bei diesem Beispiel fanden wir, dass das Verhältnis Kupfer zu Nickel fällt, das Potential an der Kathode aber steigt mit steigender Stromdichte.

(4) **Galvanische Abscheidung von Kupfer- und Cadmium-Legierungen.** Der Elektrolyt, dessen Zusammensetzung bereits beschrieben worden ist, war hier von einer gelben Farbe. Die Anoden bestanden aus zwei Kupferplatten. Die Ergebnisse sind im folgenden wiedergegeben:

Tabelle 8.

Plattennummer	Zeit in Min.	Stromdichte Amp./cm. ²	Kath. Potential	Zellenspannung	Abgesch. Metall (gr.)	Cu/Cd	Bemerkungen
20	30	0.0081	1.3280	0.80	0.1248	2.8	Bläulichweisse Farbe
19	30	0.0043	1.3300	0.60	0.0780	3.2	Gleiche Farbe
17	30	0.0029	1.3327	0.55	0.0636	3.7	„
16	30	0.0022	1.3383	0.50	0.0384	4.5	„

Zusammenfassung.

(1) Die Potentiale von Metall-Metallcyanid in Alkalicyanidlösung wurden einer Untersuchung unterzogen.

(2) Aus den erhaltenen Einzelpotentialen konnte der Verfasser die optimalen Bedingungen für die elektrolytische Abscheidung von Legierungen ermitteln.

(3) Unter Anwendung der ermittelten Daten konnte die elektrolytische Abscheidung von Legierungen mit gutem Erfolg durchgeführt werden.

Technische Hochschule, Yokohama.

UEBER DIE KAPILLARAKTIVITÄT VON DEN NORMALEN ALIPHATISCHEN DICARBONSÄUREN.

Von Bun-ichi TAMAMUSHI.

Eingegangen am 26. März 1932. Ausgegeben am 28. Mai 1932.

Einleitung. Die regelmässige Aenderung der Oberflächenspannung mit der Molekulargrösse, die als Traubesche Regel bekannt ist, wurde besonders in der Reihe der normalen aliphatischen Monocarbonsäuren ausgesprochen.⁽¹⁾ Die Regel sagt, dass, während die Molargewichte der Stoffe einer homologen Reihe eine arithmetische Reihe bilden, die spezifischen Kapillaraktivitäten eine geometrische Reihe darstellen. Langmuir⁽²⁾ gelang es diese Regel zu erklären. Nach ihm wird die Traubesche Regel folgendermassen ausgedrückt. Zwischen je zwei aufeinanderfolgenden Stoffen einer homologen Reihe besteht ein konstanter Unterschied in den Arbeiten, die erforderlich sind, um ein Mol des kapillaraktiven Stoffes aus der Oberfläche in die Lösung zu bringen, und zwar wächst diese Arbeit beim Wachsen des Molargewichtes. Solche Beziehung ist verständlich, wenn jede neu hinzukommende CH_2 -Gruppe in derselben Weise zur Wirkung gelangt wie jede vorangehende. Es leuchtet auch ein, dass dabei die Kapillaraktivität eines Stoffes mit seinem Lösebestreben zusammenhängt.

Es handelt sich nun um die Frage, ob derartige Regelmässigkeiten auch in der Reihe der normalen aliphatischen Dicarbonsäuren bestehen.

(1) Vergl. H. Freundlich, *Kapillarchemie*, vierte Auflage, Bd. 1, Leipzig (1930), s. 75.

(2) *J. Amer. Chem. Soc.*, **39** (1917), 1883.

Es ist gleichzeitig zu fragen, wie das bekannte Oszillieren der Löslichkeit sowie des Schmelzpunktes dieser Säuren⁽¹⁾ (vgl. Tabelle 1) ihre Kapillaraktivität beeinflusst. Im folgenden sollen diese Fragen teilweise beantwortet werden.

Tabelle 1.

Substanz	Formel	Schmelzpunkt	Löslichkeit g. i. 100 gr. Wasser (20°C.)
Oxalsäure	HOOC-COOH	189.5	8.6
Malonsäure	HOOC(CH ₂)COOH	133	73.5
Bernsteinsäure	HOOC(CH ₂) ₂ COOH	183	5.8
Glutarsäure	HOOC(CH ₂) ₃ COOH	97.5	63.9
Adipinsäure	HOOC(CH ₂) ₄ COOH	153	1.5
Pimelinsäure	HOOC(CH ₂) ₅ COOH	105.5	5.0
Korksäure	HOOC(CH ₂) ₆ COOH	140	0.16
Azelainsäure	HOOC(CH ₂) ₇ COOH	108	0.24

Versuche an der Oberflächenspannung der wässrigen Lösungen. Die zu den Versuchen verwendeten Dicarbonsäuren waren meistens das Präparat von Merck. Adipinsäure ist gelegentlich in meinem Laboratorium hergestellt worden.⁽²⁾ Die Oberflächenspannung wurde nach der Du Nouyschen Methode⁽³⁾ gemessen, dabei wurde die Temperatur des Messungsraums auf 15°C. gehalten und jede einmalige Messung möglich schnell, in etwa 20 Sekunden, ausgeführt. Der Mittelwert von drei bis fünf Messungen wurde aufgenommen. Die Oberflächenspannung des reinen Wassers war 106 auf der Skala der Torsionswaage, d. h. 74.6 Dyne/cm. in absoluten Einheiten. Die Konzentrationsbereiche, in denen die Versuche durchgeführt worden sind, waren bei den ersten vier Säuren 0–0.5 Mol im Liter, während sie bei den andern sehr beschränkt waren, da ihre Löslichkeit klein ist. Tabelle 2 sowie Figur 1 zeigen die Ergebnisse. In der Tabelle, bedeutet c die Konzentration, σ die Oberflächenspannung in Dyne/cm., und K eine Konstante, ueber die noch später erläutert wird.

- (1) Das merkwürdige Oszillieren des Schmelzpunktes bzw. der Löslichkeit mit der Molekulargröße in der Reihe der normalen aliphatischen Dicarbonsäuren scheint gittertheoretisch erläutert zu werden. Vgl. Müller, *Proc. Roy. Soc. A.*, **124** (1929), 317. Es wäre aber wünschenswert weitere Kenntnisse ueber die Molekülstruktur dieser homologen Stoffe zu bekommen. Die ultraviolett- sowie ultrarotspektroskopischen Untersuchungen sind in meinem Laboratorium im Gange.
- (2) Ich möchte an dieser Stelle Herrn Dr. Y. Tsuzuki fuer seine freundliche Lieferung des Versuchsmaterials herzlichst danken.
- (3) Vergl. z.B. Handbuch der Experimentalphysik, Bd. 6.

Tabelle 2.

	c	σ	K		c	σ	K
Oxal- säure	0	74.6	—	Adipin- säure	0	74.6	—
	0.12	74.6	—		0.017	71.8	2.20
	0.24	74.3	0.017		0.034	69.0	2.20
	0.36	74.0	0.022		0.050	66.2	2.25
	0.48	73.6	0.028		0.070	66.2	1.61
	Mittelwert 0.023				Mittelwert 2.06		
Malon- säure	0	74.6	—	Kork- säure	0	74.6	—
	0.048	71.1	0.977		0.0006	72.5	47.3
	0.096	70.7	0.543		0.0012	71.1	39.1
	0.144	67.2	0.689		0.0017	70.4	33.1
	0.240	65.5	0.508		Mittelwert 33.2		
	0.337	64.8	0.390				
	0.385	64.0	0.369				
	0.481	62.6	0.334				
	Mittelwert 0.544						
Bernstein- säure	0	74.6	—	Azelain- säure	0	74.6	—
	0.09	73.6	0.149		0.0005	74.0	16.1
	0.17	72.1	0.197		0.0011	72.5	25.6
	0.25	69.7	0.262		0.0016	71.8	23.5
	0.34	67.9	0.263		0.0021	70.4	26.8
	Mittelwert 0.218				0.0040	67.6	26.1
					Mittelwert 23.6		
Glutar- säure	0	74.6	—				
	0.008	74.3	0.503				
	0.019	74.0	0.423				
	0.038	73.2	0.495				
	0.076	71.8	0.494				
	0.114	71.1	0.413				
	0.152	69.0	0.494				
	Mittelwert 0.470						

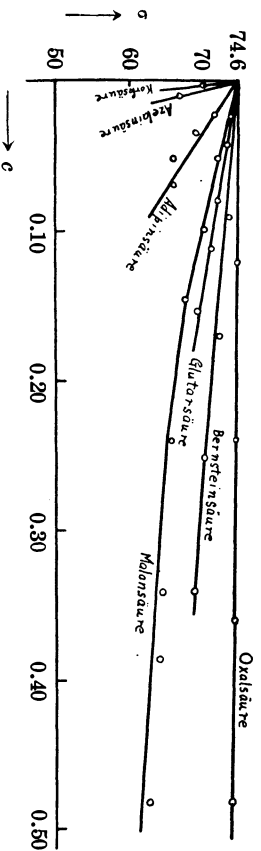


Fig. 1.

Adsorptionsversuche an Kohle. Der Adsorbens war die Mercksche Tierkohle, die stundenlang in einem halbgeschlossenen Quarzrohr ueber Mekerflamme aktiviert wurde. Man hat 30 ccm. wässrige Lösung mit 0.3 gr. Kohle geschüttelt, und deren Solutgehalt vor und nach der Adsorption titrimetrisch—eine Baryta-Lösung als Standardlösung und Bromthymol-blau als Indikator—bestimmt. Die Ergebnisse sind in der folgenden Tabelle angegeben. Die Freundlichsche Adsorptionsisotherm gilt wohl auch in diesen Fällen. Die Beziehung zwischen Balkkonzentration und der adsorbierten Menge ist in Figur 2 und 3 gezeigt. In Tabelle 3 bedeutet c die Konzentration in Mol im Liter, a die adsorbierte Menge in Millimol pro Gramm Adsorbens. Die Versuchstemperatur war 15°C.

Tabelle 3.

	c	a		c	a
Malon- säure	0.5329	5.39	Glutar- säure	0.1723	2.92
	0.3552	4.33		0.0698	2.03
	0.2333	3.71		0.0318	1.44
	0.1140	2.56			
	0.0530	1.78			
	0.0290	1.52			
Bernstein- säure	0.4713	4.59	Adipin- säure	0.09809	2.56
	0.3621	3.80		0.06468	1.94
	0.2094	3.45		0.03976	1.15
	0.0901	2.21		0.02598	0.78
	0.0286	1.09			

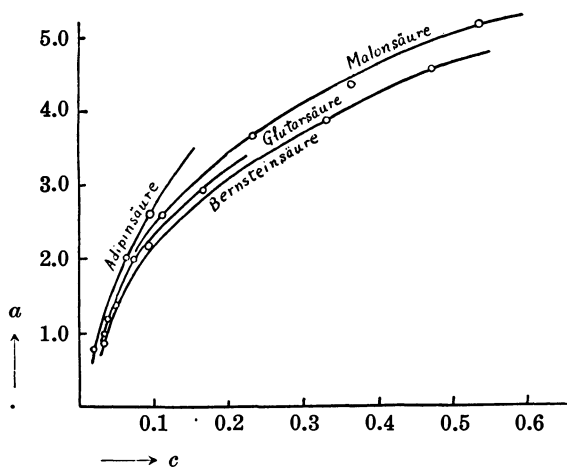


Fig. 2.

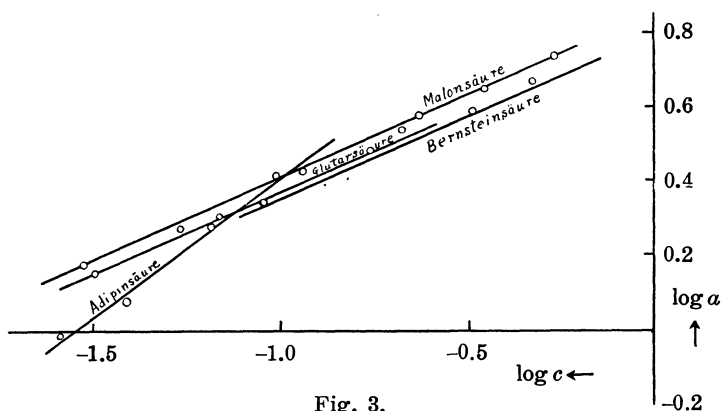


Fig. 3.

Diskussion der Resultate. Bemerkenswert ist die Stelle von Malonsäure und Glutarsäure in der Reihenfolge der Oberflächenspannungs-erniedrigung, nämlich Oxalsäure < Bernsteinsäure < Glutarsäure < Malonsäure < Adipinsäure usw. Genau dieselbe Reihenfolge ist ebenso in der Adsorbierbarkeit an Tierkohle gefunden worden. Wie kommt das, dass Malonsäure kapillaraktiver als Glutarsäure und Glutarsäure kapillaraktiver als Bernsteinsäure ist? Von dem Lösebestreben dieser Stoffe sollte man die umgekehrte Reihenfolge erwarten. Es gelang mir noch nicht diese Sachlage aufzuklären.⁽¹⁾

Lassen wir aber einstweilen Malonsäure und Glutarsäure, die, mit ungeraden Kohlenstoffatomen, auffallend starkes Lösebestreben besitzen als die andern Säuren, ausser Betracht, und vergleichen wir nur die Säuren mit geraden Kohlenstoffatomen, nämlich Oxalsäure (C₂), Bernsteinsäure (C₄), Adipinsäure (C₆) und Korksäure (C₈) miteinander, dann finden wir hierbei eine Antibasie zwischen Kapillaraktivität und Löslichkeit und auch eine regelmässige Aenderung der Kapillaraktivität mit Molekulargrösse, ueber die ich mir folgende Ueberlegung erlauben möchte.

Eine empirische Formel, die man v. Szyszkowski⁽²⁾ verdankt, drückt die Beziehung zwischen Oberflächenspannung (σ) und Konzentration (c) aus. Sie lautet:

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = b \ln \left(\frac{c}{C} + 1 \right), \dots\dots\dots (1)$$

(1) Vergl. Freundlich, loc. cit. s. 87.

(2) Szyszkowski, *Z. physik. Chem.*, **64** (1908), 385.

wobei σ_M die Oberflächenspannung des reinen Lösungsmittels, σ_L die Oberflächenspannung der Lösung bedeutet. C und b sind Konstanten. Bei kleinen Konzentrationen bekommen wir

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = b \frac{c}{C}, \dots\dots\dots (2)$$

indem wir den Logarithmus in Gleichung (1) in eine Reihe entwickeln und die höheren Glieder vernachlässigen. Gerade diese Gleichung (2) stellt die oben angegebenen Ergebnisse ueber die Aenderung der Oberflächenspannung mit der Konzentration dar. (vgl. Fig. 1) Wir setzen nun bequemlichkeitshalber

$$\frac{b}{C} = K,$$

wobei K eine andere Konstante bedeutet, so haben wir

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = Kc. \dots\dots\dots (3)$$

Wir nehmen weiter an, dass die Konstante b für alle Glieder der homologen Reihe gleich ist, und das ist doch ja wahrscheinlich.⁽¹⁾ Infolgedessen wird die Konstante K als die spezifische Kapillaraktivität bezeichnet. Die berechneten Mittelwerte von K sind in der vorhergehenden Tabelle 2 angegeben.

Bildet man den Quotienten

$$K_{n+2} / K_n$$

für je zwei aufeinanderfolgende Stoffe (mit geraden Kohlenstoffatomen), so ist dieser so gut wie konstant, und zwar hat er einen Wert von ungefähr 9.5.⁽²⁾ Es scheint somit die Traubesche Regel auch für diesen Fall zahlenmässig gültig zu sein.

Nach der Langmuirschen Theorie wird sich die spezifische Kapillaraktivität folgendermassen ausdrücken:

$$K = e^{kM}, \dots\dots\dots (4)$$

(1) Im allgemeinen verändert sich b nur wenig von Stoff zu Stoff. C ist dagegen eine für jeden Stoff charakterische Konstante und der reziproke Wert $1/C$ ist eigentlich die spezifische Kapillaraktivität genannt. Solang b unveränderlich ist, ist K d.h. b/C dem $1/C$ proportional.

(2) Korksäure ist hierbei ausgenommen, deren K verhältnismässig viel zu gross ist.

wo M das Molargewicht und k eine Konstante bedeutet. Für je zwei aufeinanderfolgende Stoffe gilt

$$K_{n+2}/K_n = e^{\frac{k(M_{n+2}-M_n)}{RT}}. \quad \dots\dots\dots (5)$$

Solang die Konzentration klein ist, haben wir nach dem Maxwell-Boltzmannschen Prinzip folgende Beziehung:

$$\frac{a}{c} = K' e^{\frac{\lambda}{RT}}, \quad \dots\dots\dots (6)$$

wobei a die adsorbierte Menge (Mol i. qcm.) in der Oberfläche, λ die Arbeit, die beim Uebergang eines Mols von der Konzentration c (Mol i. Liter) im Innern auf die Oberfläche bedeutet. K' ist eine Konstante, R die Gaskonstante und T die absolute Temperatur.

Nun ist $\frac{a}{c}$ dem K proportional. Denn, man erhält

$$-\frac{d\sigma_L}{dc} = K\sigma_M,$$

indem man die Gleichung (3) differentiiert. Und ein Vergleich mit der bekannten Gibbschen Gleichung

$$-\frac{d\sigma_L}{dc} = \frac{a}{c}RT,$$

ergibt

$$\frac{a}{c} = \frac{\sigma_M}{RT}K. \quad \dots\dots\dots (7)$$

Setzt man diese Beziehung in Gleichung (6) ein, und vereinigt die konstanten Grössen zu einer neuen Konstante K'' , dann bekommt man

$$K = K'' e^{\frac{\lambda}{RT}}.$$

Für je zwei aufeinanderfolgende Stoffe, ergibt sich

$$\frac{K_{n+2}}{K_n} = e^{\frac{1}{RT}(\lambda_{n+2}-\lambda_n)}. \quad \dots\dots\dots (8)$$

Aus Gleichungen (5) und (8) folgt

$$\lambda_{n+2}-\lambda_n = RTk(M_{n+2}-M_n).$$

Wir setzen hier den Wert

$$\frac{K_{n+2}}{K_n} = 9.5$$

in Gleichung (8) ein und berechnen den Wert von $\lambda_{n+2} - \lambda_n$ bei Temperatur $T=288$, der 1240 Grammkalorien beträgt.

Um diesen Betrag wächst also die Arbeit, die erforderlich ist, um ein Mol des kapillaraktiven Stoffes aus der Oberfläche in die Lösung zu bringen, beim Wachsen des Molargewichtes $2 \times \text{CH}_2 = 28$. Bemerkenswert ist es, dass der Betrag etwa dem Doppelten von 625 Grammkalorien, welche von Langmuir als Wert von $\lambda_{n+1} - \lambda_n$ d. h. der Betrag der Arbeit für je eine CH_2 -Gruppe in den normalen aliphatischen Monocarbonsäuren angegeben worden sind. Man könnte somit daraus schliessen, wie Langmuir für den Fall von Monocarbonsäuren getan hat, dass die Moleküle der Dicarbonsäuren in der Oberfläche des Wassers flach liegen.

In bezug auf die Ergebnisse der Adsorption an Tierkohle möchte ich noch kurz bemerken, dass die Traubesche Regel auch an der Grenzfläche zwischen Lösung und Kohle für gültig angesehen werden kann, da die Reihenfolge der Adsorbierbarkeit vollständig parallel mit derjenigen an der Grenzfläche zwischen Lösung und Luft ist.

Die Resultate von Korksäure und Azelainsäure könnte wegen sehr kleinen Konzentrationsbereiche, in denen die Untersuchungen möglich waren, für hiessige Diskussion nicht genügen. Diese Säuren sind aber auffallend kapillaraktiv und zwar Korksäure ist kapillaraktiver als Azelainsäure. Es fehlte mir zufällig Pimelinsäure und diese wurde nicht untersucht.

Das anormale Verhalten von Malonsäure sowie von Glutarsäure, auf das ich hier nicht eingehen kann, soll noch an anderer Stelle behandelt werden.

Zusammenfassung.

Es wurde die Oberflächenspannung der wässrigen Lösungen von den normalen aliphatischen Dicarbonsäuren im Konzentrationsbereiche 0–0.5 Mol i. Liter gemessen. Die Beziehung zwischen Oberflächenspannungs-erniedrigung und Konzentration ist linear, nämlich, es gilt

-
- (1) Zur Frage der Gültigkeit der Traubeschen Regel an den festen Adsorbens, siehe: E. Landt u. W. Knop, *Z. Elektrochem.*, **37** (1931), 645.

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = Kc ,$$

wobei σ_M die Oberflächenspannung des Lösungsmittels, σ_L die Oberflächenspannung der Lösung, c die Konzentration, und K die spezifische Kapillaraktivität des Stoffes bedeutet. Die Konstante K vergrößert sich in der folgenden Reihe: Oxalsäure < Bernsteinsäure < Glutarsäure < Malonsäure < Adipinsäure < Azelainsäure < Korksäure.

Was die Säuren mit geraden Kohlenstoffatomen betrifft, so gilt die Traubesche Regel. Die Arbeit, die erforderlich ist, um ein Mol des Stoffes aus der Oberfläche in die Lösung zu bringen, wächst um einen konstanten Betrag, nämlich 1240 Grammkalorien beim Wachsen des Molargewichtes $2 \times \text{CH}_2 = 28$.

Es wurde die Adsorption von Dicarbonsäuren an Tierkohle untersucht. Die adsorbierte Menge wächst in der folgenden Reihe: Bernsteinsäure < Glutarsäure < Malonsäure < Adipinsäure < Azelainsäure < Korksäure. Für alle Stoffe gilt die Freundlichsche Isotherm.

Es wurde kurz über das anormale Verhalten von Malonsäure und Glutarsäure im Zusammenhang mit ihrer Löslichkeit berichtet.

Chemical Laboratory, The Musashi Higher School,
Nakaarai, Tokyo.

SORPTION VELOCITY OF GAS BY POROUS SOLID.

By Jitsusaburo SAMESHIMA.

Received April 16th, 1932. Published June 28th, 1932.

A great number of papers are published on the sorption of gas by such porous solids as charcoal and silica gel, etc.⁽¹⁾ The author have also contributed papers on this subject.⁽²⁾ There are, however, comparatively small number of investigations concerning the kinetics of sorption. The velocity of sorption is usually measured by the decrease of gas pressure existing in contact with solid matter. Thus the pressure of gas varies according to the sorption amount. Such mode of experiment is good for the determination of the vacuum producing power or the gas collecting power of charcoal, etc. It is better, however, to measure the sorption velocity under constant pressure for the study of mechanism of sorption.

Few papers are published which describe sorption velocity under constant pressure by porous solid. Giesen⁽³⁾ measured the sorption of air, carbon dioxide and ammonia by box-wood charcoal, and Bergter⁽⁴⁾ of air, nitrogen and oxygen by coconut charcoal.

Many data on the sorption velocity have already been published by the present author and his collaborators.⁽⁵⁾ Above all, the sorption of ammonia by sugar charcoal was measured extending over six months.⁽⁶⁾ From this experiment, the author obtained the following equation,

$$x - \alpha \log t = k,$$

where x denotes the quantity of gas sorbed at time t , α and k being constants. This equation was derived as follows.

By the author's opinion, the sorption of gas by porous solid is a process of entering gas molecules into the molecular cavities of solid

-
- (1) Most of the important literatures on this subject are cited in the book: McBain, "The Sorption of Gases and Vapours by Solids" (1932).
 - (2) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289; Sameshima and Watanabe, *J. Chem. Soc. Japan*, **47** (1926), 715; Sameshima, this Bulletin, **2** (1927), 1 and 246; **4** (1929), 96 and 125; *Chemical News*, **139** (1929), 61; this Bulletin, **5** (1930), 173 and 303; **6** (1931), 165; **7** (1932), 133.
 - (3) Giesen, *Ann. Physik*, **10** (1903), 838.
 - (4) Bergter, *Ann. Physik*, **37** (1912), 472.
 - (5) Sameshima, loc. cit.; Baba, this Bulletin, **5** (1930), 190.
 - (6) Sameshima, this Bulletin, **5** (1930), 173.

and forms a homogeneous solid solution.⁽¹⁾ The entering of gas molecules into comparatively large openings in solid is accomplished quickly. Then the gas molecules begin to enter into more narrow cavities among solid molecules overcoming a great resistance. Let us assume that the resistance encounters in entering into a narrow molecular cavity is proportional to the time required for it. Thus,

$$R = At$$

where R denotes the resistance, t the time and A a constant. Moreover, we obtain the following relation assuming the velocity of sorption is inversely proportional to the resistance,

$$\frac{dx}{dt} = \frac{B}{R},$$

where x is the quantity of gas sorbed, and B another constant. We have, therefore,

$$\frac{dx}{dt} = \frac{B}{At}.$$

Integrating this equation it becomes,

$$x = \frac{B}{A} \ln t + k$$

where k is the integration constant. Substituting another constant a we obtain,

$$x = a \log t + k \quad \dots\dots\dots (I)$$

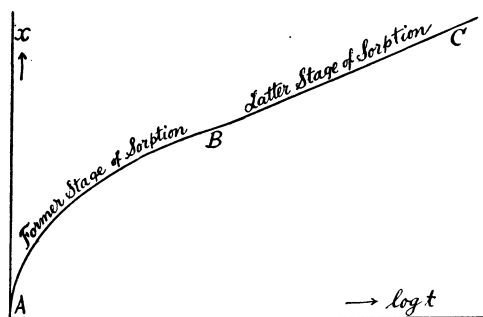


Fig. 1.

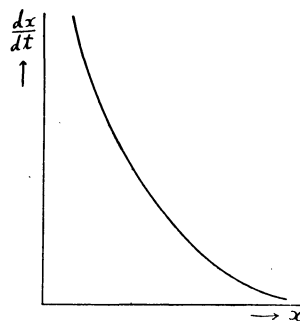


Fig. 2.

(1) Sameshima, this Bulletin, 4 (1929), 125; Chem. News, 139 (1929), 61.

Generally, the sorption velocity is expressed by a curve shown in Fig. 1, which has been drawn taking x against $\log t$. The curve converts into a straight line in the region of large t . Such a region, therefore, is expressed by Equation (I). The values of α and k can be evaluated by the slope and the height of intersection to x axis at $\log t = 0$. In the tables below, these values are given in the actual examples.

The former part of sorption, A to B in Fig. 1, cannot be expressed by Equation (I). This part corresponds to the entering of gas molecules into comparatively large openings in solid. The author proposes the following equation for this part,

$$\frac{dx}{dt} = K \frac{s-x}{x^n}$$

where s denotes the saturation amount, and K and n are constants. The value of s corresponds to the saturation value of the former part of sorption which amounts roughly to the height of B in Fig. 1. The exact value, however, cannot be obtained from the curve.

We assume, as usual, the velocity of sorption is proportional to the unoccupied space in solid, $(s-x)$. Moreover, the sorption proceeds by and by beginning with the place of greatest affinity between gas and solid. The places of great affinity will be occupied at first with great velocity, and the places of small affinity will be occupied slowly. In the later period, only the places of small affinity remains unoccupied by the gas molecule, so the sorption velocity becomes slower and slower in course of sorption. This behavior may be expressed by assuming that the velocity is inversely proportional to n th power of the occupied space x , thus $\frac{dx}{dt} \propto \frac{1}{x^n}$. The value of n is the measure of distribution of affinity between gas and solid.

We obtain, therefore, the following equation as already described.

$$\frac{dx}{dt} = K \frac{s-x}{x^n} \dots\dots\dots (II)$$

By integrating we have

$$\begin{aligned} & -s^n \ln(s-x) + n s^{n-1}(s-x) - \frac{n(n-1)}{2} s^{n-2} \frac{(s-x)^2}{2} + \dots\dots\dots \\ & + \frac{(-1)^{k-1} n! s^{n-k} (s-x)^k}{(n-k)! k!} + \dots\dots\dots = Kt + \text{const.} \end{aligned}$$

This is the general velocity equation for the former stage of sorption. The relation is expressed graphically as Fig. 2 plotting $\frac{dx}{dt}$ against x .

Now, taking the simplest case, we will assume $n=1$ in Equation (II), thus,

$$\frac{dx}{dt} = K \frac{s-x}{x} \dots\dots\dots (III)$$

By integration it becomes,

$$s-x-s \ln (s-x) = Kt+c,$$

where c denotes the integration constant. At $t=0$ the value of x is zero, so the integration constant is

$$c = s-s \ln s$$

Therefore, we have

$$s \ln \frac{s}{s-x} - x = Kt \dots\dots\dots (IV)$$

The former part of the curve in Fig. 1, from A to B , may be expressed by this equation.

Equation (IV) has been verified by experimental data. Good coincidence has been attained between calculated and observed data. Table 1 contains the data on the velocity of sorption of ammonia by sugar charcoal, the pressure of gas being 1 atmosphere and the temperature 25°C.⁽¹⁾ The first column indicates the time in minutes after the contact of ammonia to charcoal and the second the volume of gas sorbed by 0.3550 gr. recalculated to that at normal temperature and pressure. The third column of the table shows the value of K calculated by the equation

$$\frac{2.303 \times 36.17}{t} \log \frac{36.17}{36.17-x} - \frac{x}{t} = K,$$

the fourth the value of k calculated by the equation,

$$x-1.032 \log t = k,$$

the fifth the value of x calculated inversely from these equations taking $K=37.98$ and $k=35.10$ respectively, and the sixth the difference between observed (2nd column) and calculated (5th column) values of x .

(1) Sameshima, this Bulletin, **5** (1930), 173.

Table 1.

Sorption of Ammonia by Sugar Charcoal (25°C., 1 Atm.)
[Sameshima, this Bulletin, 5 (1930), 175.]

Time in min. t	Sorption amount in c.c. $x_{\text{obs.}}$	Velocity constants		Sorption calculated $x_{\text{calc.}}$	Difference $x_{\text{calc.}} - x_{\text{obs.}}$
		K	k		
0.33 0.77 1.27 1.83 2.33 3.90	22.317 24.345 32.29 34.11 35.03 35.92	37.57 20.90 ? 38.16 38.00 38.64 36.93		22.41 28.94 32.30 34.11 34.98 35.95	+ 0.09 + 4.60 + 0.01 0 - 0.05 + 0.03
10.83 21 67 140 306	36.483 36.776 37.183 37.382 37.692		35.412 35.299 35.167 35.127	36.465 36.985 37.315 37.665	- - 0.311 - 0.198 - 0.067 - 0.027
1420 1660 3065 4425 7280	38.356 38.401 38.675 38.837 39.049		35.103 35.078 35.077 35.074 35.063	38.353 38.423 38.698 38.863 39.086	- 0.003 + 0.022 + 0.023 + 0.026 + 0.037
8740 10160 13140 17310 20140	39.138 39.218 39.305 39.423 39.515		35.070 35.083 35.054 35.049 35.073	39.168 39.235 39.351 39.474 39.542	+ 0.030 + 0.017 + 0.046 + 0.051 + 0.037
23270 27450 30225 37485 41805	39.589 39.668 39.726 39.811 39.865		35.083 35.087 35.102 35.091 35.096	39.606 39.681 39.724 39.820 39.869	+ 0.017 + 0.013 - 0.002 + 0.009 + 0.004
50550 57780 63360 73550 87885	39.951 40.033 40.077 40.144 40.234		35.097 35.119 35.122 35.122 35.132	39.954 40.014 40.055 40.122 40.202	+ 0.003 - 0.019 - 0.022 - 0.022 - 0.032
103910 125290 149550 178760 208980	40.366 40.440 40.531 40.577 40.586		35.189 35.179 35.189 35.157 35.096	40.277 40.361 40.442 40.520 40.590	- 0.089 - 0.079 - 0.089 - 0.057 + 0.004
229200 279460	40.603 40.612		35.071 34.991	40.632 40.721	+ 0.029 + 0.109

$$\text{Former stage: } \frac{2.303 \times 36.17}{37.98} \log \frac{36.17}{36.17 - x} - \frac{x}{37.98} = t.$$

$$\text{Latter stage: } 35.10 + 1.032 \log t = x.$$

These results are depicted in Fig. 3 and Fig. 4. Fig. 3 shows the velocity of former stage of sorption and Fig. 4 that of latter stage of sorption. In Fig. 3 x is plotted against t while in Fig. 4 x against $\log t$. In these figures the observed data are shown by circlets and the calculated one by curves.

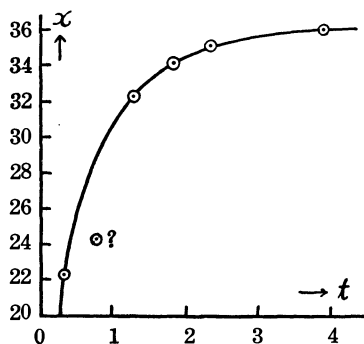


Fig. 3.

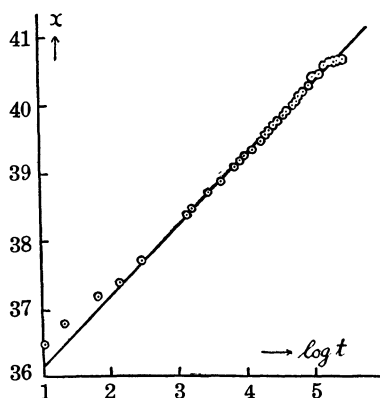


Fig. 4.

From Table 2 to Table 13 the results on various cases are given, in which, for the sake of brevity, only the values are given of time (t), the observed volume of gas sorbed (x_{obs}) and calculated value of x (x_{calc}). The calculations were done by the equations indicated under each table. The coincidence between observed and calculated values are generally good.

Table 2.

Sorption of Ammonia by Box-wood Charcoal (20°C., 488 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
1	28.	31.3
2	39.7	39.7
3	45.7	44.7
4	48.7	48.2
5	50.7	50.5
6	52.2	52.2
7	52.9	53.5
8	53.3	—
9	53.6	—
10	53.7	—
15	54.3	54.4
20	54.5	54.5
30	54.7	54.6
60	55.0	55.3
120	55.1	55.1
180	55.2	55.2
240	55.2	55.2

former stage

Table 3.

Sorption of Carbon Dioxide by Box-wood Charcoal (18.5°C., 621 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
1	18.8	18.5
2	22.3	22.8
3	25.2	25.1
4	26.4	26.5
5	27.3	27.3
6	27.6	27.5
7	27.7	27.7
8	27.8	27.8
9	27.9	27.9
10	27.9	28.0
15	28.3	28.5
20	28.7	28.7
30	29.3	29.2
60	30.4	29.9
120	30.8	30.6
180	31.1	31.0
240	31.2	31.3
300	31.2	31.5

former stage

Former stage :

$$\frac{2.303 \times 58}{13.7} \log \frac{58}{58-x} - \frac{x}{13.7} = t.$$

Latter stage :

$$53.6 + 0.7 \log t = x.$$

Former stage :

$$\frac{2.303 \times 29.3}{10.56} \log \frac{29.3}{29.3-x} - \frac{x}{10.56} = t.$$

Latter stage :

$$25.7 + 2.35 \log t = x.$$

Table 4.

Sorption of Carbon Dioxide by Box-wood Charcoal (18.2°C., 496 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
1	16.0	16.2
2	20.4	20.2
3	22.8	22.5
4	23.9	24.0
5	24.7	24.8
6	25.2	25.2
7	25.3	25.3
8	25.4	25.4
9	25.5	25.5
10	25.6	25.6
15	25.8	25.9
20	26.0	26.0
30	26.3	26.3
60	26.8	26.8
120	27.4	27.3
180	27.6	27.6
240	27.6	27.9
300	27.6	27.9

Former stage :

$$\frac{2.303 \times 27.0}{8.64} \log \frac{27.0}{27.0 - x} - \frac{x}{8.64} = t.$$

Latter stage :

$$24.0 + 1.58 \log t = x.$$

Table 5.

Sorption of Air by Coconut Charcoal (18°C., 735.6 mm.)

[Bergter, *Ann. Physik*, **37** (1912), 482.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.75	16.31	—
1	17.15	—
2	18.45	18.47
3.67	19.27	19.14
5	19.56	19.48
7	19.87	19.85
9	20.09	20.06
10	20.23	20.25
13	20.49	20.54
15	20.62	20.70
20	20.93	21.02
25	21.17	21.27
30	21.47	21.47
40	21.78	21.78
50	22.01	22.03
60	22.28	22.23

Latter stage :

$$17.7 + 2.55 \log t = x.$$

Table 6.

Sorption of Ammonia by Silica
Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, 7 (1932), 134.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.5	29.00	28.84
1	35.14	35.23
2	40.19	40.36
5	43.29	43.19
10	43.64	43.72
20	43.96	43.94
185	44.64	44.63
1470	45.26	45.28
7315	45.87	45.78
17370	46.01	46.05
33225	46.26	46.25
77760	46.53	46.52

Former stage :

$$\frac{2.303 \times 43.5}{37.0} \log \frac{43.5}{43.5-x} - \frac{x}{37.0} = t.$$

Latter stage :

$$43.0 + 0.72 \log t = x.$$

Table 7.

Sorption of Ammonia by Silica
Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, 7 (1932), 134.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.5	29.93	29.66
1.17	37.30	37.25
2	41.11	40.93
4	42.94	43.11
6	43.20	43.20
10	43.39	43.38
15	43.52	43.51
30	43.76	43.75
50	43.96	43.92
135	44.27	44.25
280	44.48	44.50
1585	45.02	45.08
11520	45.85	45.75

Former stage :

$$\frac{2.303 \times 43.5}{40.3} \log \frac{43.5}{43.5-x} - \frac{x}{40.3} = t.$$

Latter stage :

$$42.6 + 0.775 \log t = x.$$

Table 8.

Sorption of Carbon Dioxide by
Silica Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, **7** (1932), 135.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.5	4.66	4.65
1	5.03	5.17
2	5.38	5.38
5	5.56	5.60
10	5.66	5.66
60	5.82	5.81
255	5.93	5.93
1380	6.08	6.07
2995	6.16	6.13
11490	6.27	6.24
34550	6.34	6.34
82050	6.40	6.40

Table 9.

Sorption of Ammonia by Opal
(25°C., 1 Atm.)

[Sameshima, this Bulletin, **6** (1931), 168.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.5	2.52	—
2	3.07	2.93
10	3.71	3.68
30	4.20	4.20
60	4.52	4.52
120	4.84	4.84
240	5.17	5.17
1460	5.99	6.02
4320	6.55	6.52

$$2.60 + 1.08 \log t = x.$$

Former stage :

$$\frac{2.303 \times 5.4}{12.0} \log \frac{5.4}{5.4 - x} - \frac{x}{12.0} = t.$$

Latter stage :

$$5.47 + 0.19 \log t = x.$$

Table 10.

Sorption of Ammonia by Diatomaceous Earth (25°C., 1 Atm.)

[Sameshima, this Bulletin, 6 (1931), 165.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.5	11.69	—
2	14.20	14.87
5	15.46	15.43
10	15.92	15.86
30	16.61	16.54
60	16.97	16.97
120	17.33	17.39
240	17.67	17.82
1560	18.86	18.97
4330	19.57	19.60
7370	19.93	19.93
11635	20.21	20.21
18850	20.47	20.51

$$14.44 + 1.42 \log t = x.$$

Table 12.

Sorption of Carbon Dioxide by Chabazite (25°C., 768.9 mm.)

[Baba, this Bulletin, 5 (1930), 194.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.42	23.3	—
1	36.8	—
1.5	41.6	42.0
2	44.1	43.5
3	45.9	45.5
5	47.8	48.0
10	51.0	51.5
20	54.3	55.0
42	59.1	58.7
60	60.9	60.5
120	64.2	63.9

$$40.0 + 11.5 \log t = x.$$

Table 11.

Sorption of Ammonia by Chabazite (25°C., 1 Atm.)

[Sameshima, this Bulletin, 4 (1929), 101.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.3	115.6	119.0
1	149.1	148.5
2.5	181.7	181.9
5	194.9	194.9
10	197.2	197.1
30	198.4	198.0
68	198.5	198.6
270	199.9	199.6
1430	200.4	200.8

Former stage :

$$\frac{2.303 \times 198}{126} \log \frac{198}{198 - x} - \frac{x}{126} = t.$$

Latter stage :

$$195.4 + 1.73 \log t = x.$$

Table 13.

Sorption of Carbon Dioxide by Chabazite (25°C., 772 mm.)

[Baba, this Bulletin, 5 (1930), 195.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.45	38.6	—
2	70.4	—
3	75.1	75.5
5	77.6	77.5
10	80.2	80.0
20	82.4	82.6
45	85.3	85.5
80	87.8	87.7
120	89.3	89.2
180	90.8	90.7
1200	96.2	97.7

$$71.5 + 8.5 \log t = x.$$

Summary.

1. The sorption by porous solid of gas under constant pressure and temperature proceeds, generally, in two stages. The mechanisms of sorption of each stage are described.

2. The velocity of the former stage is expressed by the equation

$$\frac{dx}{dt} = K \frac{s-x}{x^n}$$

where x denotes the amount of gas sorbed at time t , and K , s and n are constants. In the simplest case where $n=1$, this equation is integrated in the following form,

$$\frac{s}{t} \ln \frac{s}{s-x} - \frac{x}{t} = K.$$

3. The velocity of the latter stage of sorption is expressed by

$$x - \alpha \log t = k$$

where α and k are constants.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

POTENTIOMETRIC TITRATION OF SODIUM AND POTASSIUM FERROCYANIDE.

By Kosaku MASAKI.

Received March 8th, 1932. Published June 28th, 1932.

On the potentiometric titration of potassium and sodium ferrocyanide with metallic salts were already reported by many investigators. In 1915, Knauth⁽¹⁾ was studied on the potentiometric titration of potassium ferrocyanide with zinc salt by using zinc electrode as the indicator electrode and he showed that the titration might be made by the potentio-

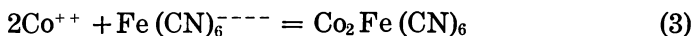
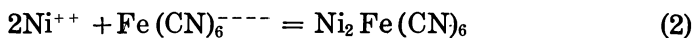
(1) *Dissert. Dresden* (1915).

metric method. This was confirmed quite independently by Bischowsky,⁽¹⁾ and G. Hedrich⁽²⁾ concluded that the method gave highly accurate results by the special study of this titration and also Kolthoff and Verzijl⁽³⁾ was done a special study of the absolute accuracy of the method. Treadwell and Chervet⁽⁴⁾ stated that the composition of a metal ferrocyanide depends upon the alkali metal of the ferrocyanide and they found that in titrating zinc with potassium ferrocyanide the composition of ferrocyanide was $K_2Zn_3[Fe(CN)_6]_2$, while with sodium ferrocyanide $Zn_2Fe(CN)_6$.

Hedrich also stated that the break in potential does not occur exactly at the point corresponding to the formation of $K_2CdFe(CN)_6$ in the titration of a cadmium salt with potassium ferrocyanide. Müller and Gabler⁽⁵⁾ investigated the titration of lead with ferrocyanide and also they obtained good results when the lead concentration is larger than 0.01 molal. Hedrich studied the titration of potassium ferrocyanide with cupric salt and Niemz⁽⁶⁾ with silver salt at 70°C. But Müller showed that the ferrocyanide titration is not suitable for the determination of silver and copper.

In this investigation the potentiometric titration of potassium and sodium ferrocyanide with mercuric chloride, nickel sulphate and cobalt sulphate by using platinum electrode as the indicator electrode at 25°C. were employed.

In the titration of potassium and sodium ferrocyanide with metallic salts, the reactions take place as follows.



In the above reactions the potential is governed by the following equation by adding a little ferricyanide to the solution and taking bright platinum as the indicator electrode.

$$E = e + 0.0591 \log \frac{[Fe(CN)_6^{---}]}{[Fe(CN)_6^{----}]} \quad (4)$$

(1) *J. Ind. Eng. Chem.*, **9** (1917), 668.

(2) *Dissert. Dresden* (1915).

(3) *Rec. Trav. Chim.*, **43** (1924), 380; *Z. anorg. Chem.*, **132** (1923), 318.

(4) *Helv. Chim. Acta.*, **5** (1922), 633.

(5) *Z. analyt. Chem.*, **62** (1923), 29.

(6) *Dissert. Dresden* (1920).

From the reactions (1), (2) and (3), we have next equation,

$$[\text{Fe}(\text{CN})_6^{---}] = \frac{S_{\text{Me}_2\text{Fe}(\text{CN})_6}}{[\text{Me}^{++}]^2}$$

By substituting this value in equation (4) and taking $[\text{Fe}(\text{CN})_6^{---}]$ as a constant, we have

$$E_{\text{Fe}(\text{CN})_6} = e' - 0.0591 \times 2P_{\text{Me}}$$

Therefore we knew that the ferrocyanide electrode responds to the concentration of metal ions ($\text{Ni}^{++}, \text{Co}^{++}, \text{Hg}^{++}$).

Experimental Part.

Potassium and sodium ferrocyanide, potassium and sodium ferricyanide, mercuric chloride, nickel sulphate and cobaltous sulphate used were of Kahlbaum's. These salts were purified by recrystallization. One-tenth molal solutions of these salts were prepared very carefully.

(1) Titration by Sodium Ferrocyanide with Mercuric Chloride.
10 C.c. of one-tenth molal solution of sodium ferrocyanide and 1 c.c. of one-tenth molal sodium ferricyanide were taken in the half cell and this solution diluted to 100 c.c. with conductance water, and then the half cell was connected with decinormal calomel electrode with decinormal salt bridge. After the cell was kept in a thermostat at $25 \pm 0.05^\circ\text{C}$. for one hour, the electromotive forces of the cell were measured. Then a c.c. of mercuric chloride solution was added from the burette into the half cell and stirred, and then the electromotive force of the cell was measured. The results are summarized in Table 1.

In the above titration, when 5 c.c. of mercuric chloride solution were added to sodium ferrocyanide solution, the solution took green colour. As it can be seen in Table 1 and Fig. 1, we obtained 20.05 c.c. as the end point.

(2) Titration by Mercuric Chloride with Sodium Ferrocyanide.
40 C.c. of one-tenth molal solution of mercuric chloride was taken and this solution was diluted to 100 c.c. with conductivity water, and then the titration was done by the one-tenth molal solution of sodium ferrocyanide. The results are summarized in Table 2.

In Table 2 and Fig. 1, we obtained 20.02 c.c. as the maximum point. During the titration, the solution changed yellow to blueish green. We had very good agreement with each other.

Table 1.

C.c. of HgCl_2 a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	—0.04616	1150
2	.02316	997
3	.01319	519
4	.00800	172
5†	.00628	158
6	.00470	162
7	.00632	104
8	.00736	917
9	.01653	939
10	.02592	333
11	.02925	185
12	.02740	744
13	.03484	484
14	.03000	150
15	.02850	225
16	.02625	1000
17	.01625	763
18	.00862	1535
19	+.00125	3699
20	.04920	3918*
20.5	.06605	1850
21	.07530	1020
21.5	.08040	860
22	.08470	610
22.5	.08775	450
23	.09000	384
24	.09384	316
25	.09700	808
30	.13742	400
35	.15742	250
38	.16745	327
40	.17400	

† Green colour.

* Maximum point.

Experimental value 20.05 c.c.

Table 2.

C.c. of $\text{Na}_4\text{Fe}(\text{CN})_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.43690	9645
1	.34045	2045
2	.32000	1150
3	.30850	850
4	.30000	800
5	.29200	680
6	.28520	425
7	.28095	829
8	.27266	726
9	.26540	1394
10	.25146	497
11	.24649	729
12	.23920	955
13	.22965	1190
14	.21775	1425
15	.20350	1990
16	.18360	2000
17	.16360	2730
18	.13630	3660
18.5	.11800	4470
19	.09395	4690
19.5	.07050	4732
20	.04574	5038*
20.5	.02055	1250
21	.01430	954
21.5	.00953	808
22	.00549	549
23	.00000	1520
24	— .01520	345
25	.01865	541
26	.02406	228
30	.03320	69
35	.03665	41
40	.03870	

* Maximum point.

Experimental value 20.02 c.c.

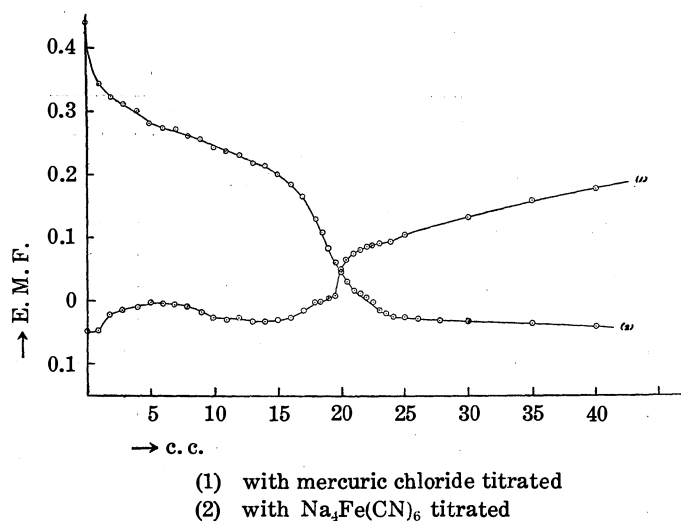


Fig. 1.

(3) **Titration by Nickel Sulphate with Potassium Ferrocyanide.** 20 C.c. of one-tenth molal solution of nickel sulphate was taken in the half cell and diluted to 100 c.c. with conductivity water and then titrated with 0.1 molal solution of potassium ferrocyanide after the cell was kept in a thermostat at $25 \pm 0.05^\circ\text{C}$. for one hour. The results are summarized in Table 3. In this case we obtained 10.06 c.c. at the maximum point. The ratio of Ni to ferrocyanide is 1.98:1.

(4) **Titration by Potassium Ferrocyanide with Nickel Sulphate.** 5 C.c. of one-tenth molal potassium ferrocyanide solution and 0.5 c.c. of one-tenth molal solution of potassium ferricyanide were taken in the half cell and the solution diluted to 100 c.c. and then this solution titrated with nickel sulphate solution. The results are shown in Table 4. As it can be seen in the Table 4 and Fig. 2, we obtained 9.95 c.c. as the maximum point. This value is very good agreement with other.

(5) **Titration by Potassium Ferrocyanide with Cobaltous Sulphate.** 5 C.c. of one-tenth molal solution of potassium ferrocyanide and 0.5 c.c. of one-tenth molal solution of potassium ferricyanide were taken and the mixed solution was diluted to 100 c.c. with conductivity water, and then titrated with one-tenth molal solution of cobaltous sulphate. The results are summarized in Table 5. As it can be seen in the Table 5 and Fig. 3, we obtained 10.02 as the maximum point. Therefore the ratio of Co to ferrocyanide is 1:2.004.

Table 3.

C.c. of $K_4Fe(CN)_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	-0.05585	3190
1	.02395	1009
2	.01386	706
3	.00680	182
4	.00498	300
5	.00198	136
6	.00062	37
7	.00025	—
8	.00025	255
8.5	.00280	368
9	.00464	600
9.5	.00764	800
10	.01164	884*
10.5	.01606	700
11	.01956	344
11.5	.02128	268
12	.02262	45
13	.02307	93
14	.02400	50
15	.02450	125
16	.02420	100
17	.02320	32
18	.02288	179
19	.02467	80
20	.02547	222
21	.02767	200
22	.02967	513
23	.03480	—
24	.03480	100
25	.03580	315
26	.03895	177
27	.04072	200
28	.04272	106
29	.04378	99
30	.04477	

* Maximum point.
Experimental value 10.06 c.c.

Table 4.

C.c. of Na_2SO_4 a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	-0.000225	3375
1	.003600	2220
2	.005820	285
3	.005635	8310
3.5	.009690	2000
4	.008690	360
4.5	.008370	1368
5	.009554	4278
5.5	.007415	4652
6	.005089	2178
6.5	.004000	8000
7	.000000	9000
7.5	+0.004500	9000
8	.003000	10000
8.5	.014000	11100
9	.019550	11150
9.5	.025125	13750*
10	.032000	13020
10.5	.038510	10980
11	.044000	6000
11.5	.047000	8000
12	.051000	6000
13	.057000	6111
14	.063111	2689
15	.065800	—
16	.065800	2000
17	.067800	3800
18	.068184	1331
19	.069525	—
20	.069525	

* Maximum point.
Experimental value 9.95 c.c.

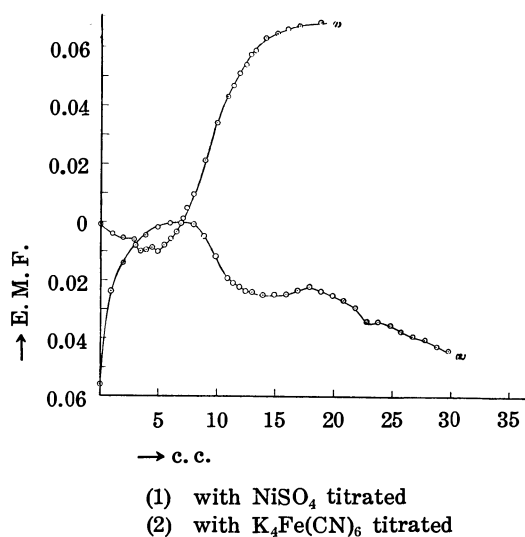


Fig. 2.

(6) **Titration by Cobaltous Sulphate with Potassium Ferrocyanide.** 20 C.c. of one-tenth molal cobaltous sulphate solution were taken and diluted to 100 c.c. with conductance water and then titrated one-tenth molal potassium ferrocyanide at $25 \pm 0.05^\circ\text{C}$. We obtained the results shown in Table 6. We obtained 9.98 c.c. as the maximum point from the Table 6 and Fig. 3. Hence we knew that the ratio of Co to ferrocyanide is corresponding to 1:1.996.

(7) **Titration by Potassium and Sodium Ferrocyanide with Ferric Chloride and Silver Nitrate.** As already mentioned above, we studied the potentiometric titration by potassium and sodium ferrocyanide with metallic salts. In the following experiments, the potentiometric titration compared with potassium and sodium ferrocyanide by the solutions of ferric chloride and silver nitrate at the same condition or different condition.

Ferric chloride and silver nitrate used were of Kahlbaum's. These salts were purified by washing with conductance water and then each 0.1 molal solution was prepared very carefully.

At first the potentiometric titration was carried out with 0.1 molal solution of potassium and sodium ferrocyanide by 0.1 molal solution of ferric chloride and at the second by 0.1 molal solution of silver nitrate. Each 10 c.c. of 0.1 molal solution of potassium and sodium

Table 5.

C.c. of CoSO_4 a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	-0.00108	49
1	.00157	27
2	.00185	185
3	.00000	—
4	.00000	102
5	+0.00102	274
6	.00376	124
7	.00500	300
8	.00800	200
8.5	.00900	210
9	.01010	380
9.5	.01200	390
10	.01395	510*
10.5	.01750	300
11	.01900	200
11.5	.02000	150
12	.02150	120
13	.02270	243
14	.02513	282
15	.02795	165
16	.02950	304
17	.03254	200
18	.03454	117
19	.03571	168
20	.03739	201
25	.03940	60
30	.04000	

* Maximum point.

Experimental value 10.02 c.c.

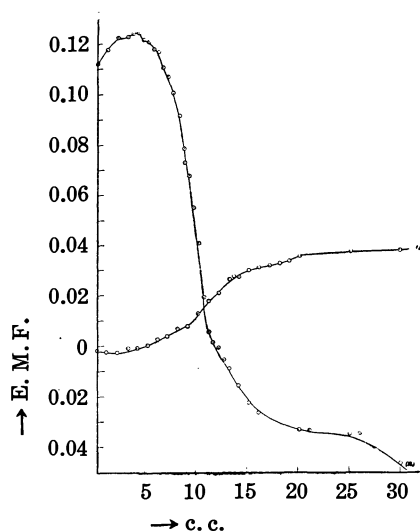
Table 6.

C.c. of $\text{K}_4\text{Fe}(\text{CN})_6$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.11565	535
1	0.12100	560
2	0.12660	—
3	.12660	130
3.5	.12790	—
4	.12790	550
4.5	.12515	180
5	.12425	540
5.5	.12155	310
6	.12000	1280
6.5	.11360	580
7	.11070	1410
7.5	.10365	1900
8	.09415	2850
8.5	.08090	2180
9	.07000	2590
9.5	.05705	4902*
10	.03254	2508
10.5	.02000	2800
11	.00600	800
11.5	.00200	400
12	.00000	1000
12.5	-0.00500	800
13	.00900	700
14	.01600	750
15	.02350	430
16	.02780	163
20	.03434	53
25	.03550	253
30	.04765	

* Maximum point.

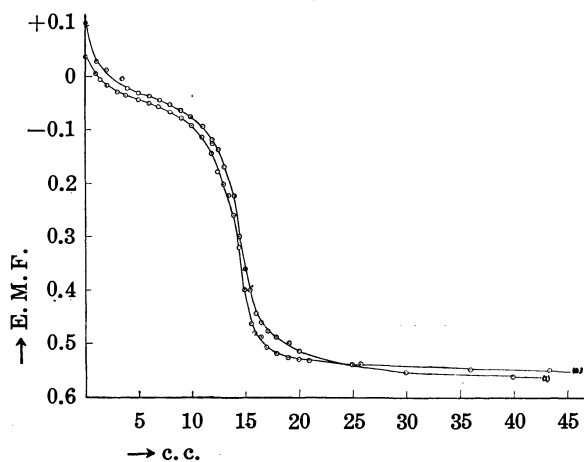
Experimental value 9.98 c.c.

ferrocyanide and 1 c.c. of 0.1 molal solution of potassium and sodium ferricyanide were taken and these solutions diluted to 100 c.c. with conductance water and then each solution was titrated by 0.1 molal solution of ferric chloride. The platinum electrode was used as the indicator electrode. The results are summarized as Tables 7 and 8.



- (1) with CoSO_4 titrated
(2) with $\text{K}_4\text{Fe}(\text{CN})_6$ titrated

Fig. 3.



- (1) with $\text{Na}_4\text{Fe}(\text{CN})_6$ titrated
(2) with $\text{K}_4\text{Fe}(\text{CN})_6$ titrated

Fig. 4.

Table 7.

Titration by $K_4Fe(CN)_6$ with
Ferric Chloride

C.c. of $FeCl_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.04566	
1	.01106	3460
2	—0.01075	31
3	.02349	1274
4	.03132	783
		694
5	.03826	714
6	.04540	866
7	.05406	818
8	.06224	1096
9	.07320	1560
		1906
10	.08880	3486
11	.10786	3286
12	.14272	4070
12.5	.17555	4564
13	.19590	7816
		12004
13.5	.21872	16000*
14	.25780	13216
14.5	.31782	3220
15	.39782	1900
15.5	.46390	3644
		1038
16	.48000	850
16.5	.48950	175
17	.50772	261
18	.51810	69
19	.52660	27
21	.53010	
26	.54132	
36	.54825	
46	.55000	

* Maximum point
Experimental value 14.62 c.c.

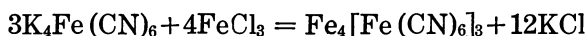
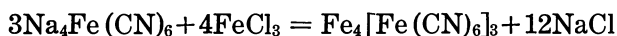
Table 8.

Titration by $Na_4Fe(CN)_6$ with
Ferric Chloride

C.c. of $FeCl_3$ a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.10500	
1	.03523	6977
2	.01787	1736
3	.00210	1577
4	—0.01775	1985
		896
5	.02671	659
6	.03330	670
7	.04000	972
8	.04972	973
9	.05945	1435
		1620
10	.07380	2570
11	.09000	3450
12	.11570	6520
12.5	.13295	5474
13	.16555	5196
		16000*
13.5	.19292	12302
14	.21890	8658
14.5	.29890	8000
15	.36041	4600
15.5	.40370	2340
		1610
16	.44370	1355
16.5	.46670	1514
17	.47840	1266
18	.48645	412
19	.50000	200
		111
20	.51514	
21	.52780	
25	.54450	
30	.55450	
40	.56566	

* Maximum point
Experimental value 14.60 c.c.

As it was shown in Tables 7 and 8 and Fig. 4, the electromotive force in the case of sodium ferrocyanide was very little greater than that of potassium ferrocyanide before 25 c.c. of ferric chloride solution were added to potassium and sodium ferrocyanide solution, but after 25 c.c. of ferric chloride solution were added to each solution, the former electromotive force was a little lower. However the maximum value of each case was nearly same. That is, the value for sodium ferrocyanide was 14.60 c.c. and for potassium ferrocyanide 14.62 c.c. Therefore each reaction will take place as follows.



The following potentiometric titrations were carried out by the different conditions. That is, 20 c.c. of 0.1 molal solution of sodium ferrocyanide and 10 c.c. of 0.1 molal solution of potassium ferrocyanide were taken and then 1 c.c. of 0.1 molal solution of sodium ferricyanide and potassium ferricyanide were added to each solution. These solutions were titrated with 0.1 molal solution of silver nitrate. The results are summarized in Tables 9 and 10. As it is shown in Fig. 5, each curve was of the same type and we obtained 39.35 c.c. and 78.80 c.c. at the above titration. Therefore the difference of c.c. at the maximum

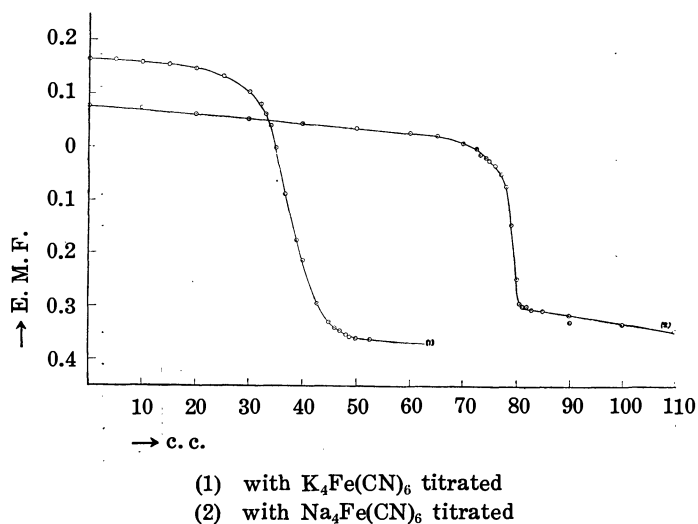


Fig. 5.

Table 9.
Titration by $\text{Na}_4\text{Fe}(\text{CN})_6$ with
Silver Nitrate

C.c. of AgNO_3 a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.07441	4
10	.07397	147
20	.05925	82
30	.05104	10
40	.04000	47
50	.03525	78
60	.02740	133
65	.02074	214
70	.01000	500
72	.00000	1580
73	−0.01580	698
74	.02278	367
75	.02645	1020
76	.03665	1171
77	.04836	1039
77.5	.05875	2770
78	.07260	6774
78.5	.10647	10878*
79	.16086	9698
79.5	.20935	8000
80	.24935	7890
80.5	.28880	2280
81	.30020	198
81.5	.30119	—
82	.30119	475
83	.30594	—
84	.30594	—
85	.30594	210
90	.31745	170
100	.33445	131
110	.34760	

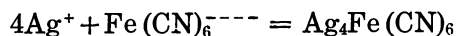
* Maximum point
Experimental value 78.80 c.c.

Table 10.
Titration by $\text{K}_4\text{Fe}(\text{CN})_6$ with
Silver Nitrate

C.c. of AgNO_3 a	E. M. F. b	$\frac{\Delta b}{\Delta a}$
0	0.16385	90
5	.15934	80
10	.15530	53
15	.15265	78
20	.14875	450
25	.12846	465
30	.10520	1090
32	.08340	2128
33	.06212	3132
34	.03080	3080
35	.00000	3730
36	−0.03730	5045
37	.08775	5191
38	.13966	5468
38.5	.16700	5632
39	.19516	6778*
39.5	.22905	4000
40	.24905	2164
43	.31399	1147
45	.33694	901
46	.34595	215
47	.34810	760
48	.35655	789
49	.36444	—
50	.36444	

* Maximum point
Experimental value 39.35 c.c.

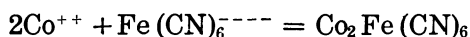
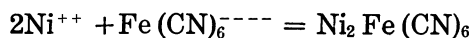
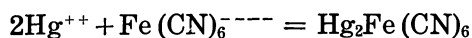
point was 0.1 c.c. and also the ratio of silver to ferrocyanide is corresponding to 1:3.935 or 1:3.940. Hence we knew that the reaction takes place in each case as follows.



Summary.

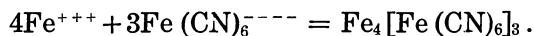
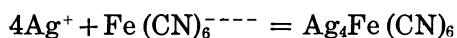
(1) The potentiometric titrations of potassium and sodium ferrocyanide with mercuric chloride, nickel sulphate and cobaltous sulphate by using platinum electrode as an indicator electrode were studied at 25°C.

(2) From the above titration we found that the reactions take place as follows.



(3) Also the potentiometric titrations were compared with potassium and sodium ferrocyanides by ferric chloride and silver nitrate solution at the same condition or different conditions, and a very good agreement was found with each other.

(4) In this titration we found that the reaction takes place as reported already by Niemz⁽¹⁾ at the case of silver and in other case as follows:



Yokohama Higher Technical School, Yokohama.

(1) Niemz, Dissert. Dresden (1920).

DISPERSITY OF CATALYST AND CATALYTIC ACTIVITY.

By Kiyoshi YOSHIKAWA.

Received May 9th, 1932. Published June 28th, 1932.

A most simple case of mixed catalysts is that in which a mixture of two substances, the one catalytically active and the other inert, forms a catalyst. In hydrogenation catalysis, a catalyst composed of nickel with an irreducible oxide such as kieselguhr, alumina, magnesia, etc. may be cited as an example. The name promoters may be given to these oxides, when the addition of a small quantity of them greatly increases the catalytic activity of nickel. The oxides may be termed carriers or supports, when nickel is distributed on a large quantity of them, the activity being not materially enhanced. It is evident, however, that to class these oxides either as promoters or as carriers is not always possible, because no decisive line of demarcation can be drawn between them. The author has studied the hydrogenation of acetylene using the nickel-kieselguhr and palladium-kieselguhr catalysts. Attention has been devoted to the modification of the catalytic activity produced by admixture with inert substance. The quantity of kieselguhr added to the catalytic agent has considerable influence on the activity of the resulting catalyst. In the presence of nickel alone and with excess of hydrogen, acetylene is hydrogenated completely to ethane. By passage over nickel or palladium distributed on a suitable amount of kieselguhr, acetylene is hydrogenated exclusively to ethylene. The composition of the products depends on the relative proportion of nickel and kieselguhr or palladium and kieselguhr. These results suggest a possible mechanism of one case of promoter and carrier actions and on the other hand, a method of selective hydrogenation of acetylene to ethylene.

(1) **A Possible Mechanism of One Case of Promoter and Carrier Actions.** The phenomenon which is met with, namely the markedly selective action of catalysts produced by varying the dispersity of the catalytic agent on an inert substance, can not be explained from the standpoint of the problem of the quantity of a catalytic agent. This can hardly be due simply to the diminution in the amount of a catalyst, since the prolonged contact with a catalyst can not cause the production of ethane. In order to offer the explanation, the author assumes the co-activation of neighbouring active centres on the catalytic surface

by the heat of reaction. A surface of catalyst may present centres of various degrees of activeness. At the start of a catalytic reaction, the centre of maximum activity, the point A, on the surface is activated and the reaction takes place at first on the point A. The reaction is exothermic and the heat of reaction may excite the neighbouring active point B and the reaction occurs on the point B. The heat of the reaction may excite not only the new active point C but also the original active point A, which is further stimulated. Thus the co-activation of active centres is achieved and the proportion of stimulated active points increased and the reaction correspondingly accelerated. After the attainment of equilibrium between accumulation and loss of heat, the reaction proceeds with constant velocity. Now the case may be considered in which a catalytically active substance is spread on a relatively large amount of non-catalytic material. If the dispersity of the catalytic agent is sufficiently large, the distance between the neighbouring active points on the surface may be long enough to disable the efficient co-activation, so that the catalytic centres can not display their full activities. There may be cases where the hydrogenation of acetylene to ethylene is possible but the hydrogenation to ethane is impossible. In most cases carriers are employed on purpose to increase the surface area of catalysts and to gain the superior activity. In this work the extreme case has been discussed in which the extent of distribution of catalytic metal on carriers is so great that the restriction of the activity can be observed. At the other extreme, the case in which a metal catalyst is admixed with a minute amount of inert oxides, may be considered. In such a case, the distance between the active points is nearly the same as that on the pure metal. The presence of an inert oxides, which is a bad conductor of heat, interspersed among the active centres, favours the accumulation of the reaction heat. The effect is the equivalent of an extremely high local temperature. Therefore, the co-activation of active centres being enhanced, the reaction velocity is greatly increased. The cases in which a metallic catalyst is stimulated by the presence of traces of irreducible oxides are very numerous and in the case where the reaction is a simple addition of hydrogen, the primary function of the promoter action may be regarded as the enhanced co-activation of active centres by the heat of reaction.

The author arrives at the conclusion with regard to the modification of a straight hydrogenation process—the simple addition of hydrogen at an unsaturated linkage—in presence of a metallic catalyst, an inert irreducible oxide such as kieselguhr, alumina, magnesia, etc. being em-

ployed as the promoter and as the carrier, that the stimulation and the restriction of catalytic activity can be satisfactorily explained on the basis of enhanced and unfavoured co-activation of active centres by the heat of reaction.

(2) **Hydrogenation of Acetylene to Ethylene.** In a series of investigations of von Wilde⁽¹⁾, Sabatier⁽²⁾, and more recently Morris⁽³⁾ it was shown that acetylene was easily hydrogenated to ethane, ethylene and liquid products in presence of metallic catalysts. Paal⁽⁴⁾ and Ross⁽⁵⁾ have investigated the hydrogenation to get ethylene and they were able to obtain the product containing 80% ethylene, the former employing colloidal palladium shaken with water, the latter in presence of nickel catalyst. Much attention has been given to the problem of preparing ethylene by the hydrogenation of acetylene, and several patents have been claimed for the technical hydrogenation. The author observed that acetylene was readily hydrogenated to ethylene by the employment of the palladium catalysts distributed on the proper amount of kieselguhr (500-1500 parts of kieselguhr added to one part of palladium). With equal volumes of acetylene and hydrogen the product contains 90% ethylene and 2-3% saturated hydrocarbons.

Experimental.

Acetylene was prepared by the action of water on calcium carbide. The removal of the impurities was accomplished by the method described in Vanino's "Präparativen Chemie." For the experiments with nickel catalysts, acetylene was solidified with liquid air and subjected to a fractional distillation. To poisons, nickel is more sensitive than palladium and without this treatment no satisfactory results were obtained. Hydrogen was obtained from cylinder of commercial electrolytic hydrogen and no attempt was made to remove the impurities except to bubble the gas through potassium hydroxide solution.

Nickel-kieselguhr catalyst was prepared by the reduction of nickel oxide admixed with kieselguhr, which was obtained by the calcination of the mixture of nickel nitrate and kieselguhr. Palladium-kieselguhr catalyst was prepared from palladium chloride solution, into which

(1) von Wilde, *Ber.*, **7** (1874), 352.

(2) Sabatier et Senderens, *Compt. rend.*, **128** (1899), 1173; **130** (1900), 1559.

(3) Morris and Reyerson, *J. Phys. Chem.*, **31** (1927), 1332.

(4) Paal und Hoheneggen, *Ber.*, **48** (1915), 275.

(5) Ross, Culbertson and Parsons, *J. Ind. Eng. Chem.*, **13** (1921), 775.

kieselguhr was added, by reduction to metal with formaldehyde.⁽¹⁾ The solution was heated on water-bath until the precipitation of palladium was completed and then filtered. For palladium catalysts, commercial kieselguhr was used with no further purification and for nickel catalysts kieselguhr was purified by boiling with hydrochloric acid solution.

The experiments were carried out by the flow method. The apparatus used is represented in Fig. 1. A mixture of acetylene and

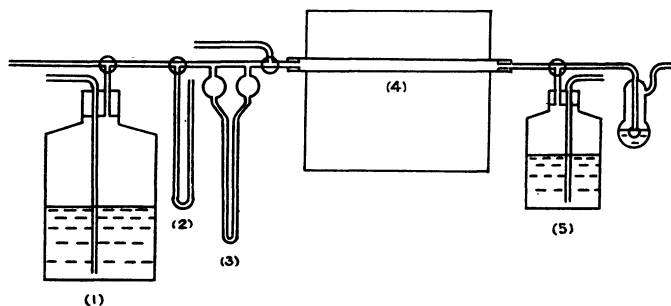


Fig. 1.

hydrogen stored in the reservoir (1) was introduced through the manometer (2) and the flowmeter (3) into the catalyst tube (4) placed in a gas furnace. The tube was made of glass, 46 cm. long and 1.4 cm. in diameter. The temperature was indicated by the thermometer placed outside the tube. The reaction products were collected into the reservoir (5). The reservoirs (1) and (5) were three litre and one litre bottles respectively and saturated sodium chloride solution was used as a confining liquid. A U-glass tube, 1.5 cm. in diameter, was occasionally used as a catalyst tube for the experiments run at the temperatures below 130°C. The tube was filled with the catalyst supported on granules of quartz and immersed in a glycerin-bath. In carrying out the hydrogenation, the catalyst tube was heated to the desired temperature, hydrogen being streamed into the tube. And the mixture of acetylene and hydrogen in the reservoir (1) was passed over the catalyst. When about one litre of the gases was passed, it was felt that the system had reached a steady state. Then the product was collected into the reservoir (5) and the extent of hydrogenation was determined by the analysis of the product.

(1) Willstätter und Waldschmidt-Leitz, *Ber.*, **54** (1921), 123.

Analyses of acetylene and ethylene were carried out according to the method of Treadwell⁽¹⁾ modified by Fujio⁽²⁾. Acetylene, ethylene and heavy hydrocarbons were determined by the absorption with the solution of mercuric cyanide, mercuric nitrate and fuming sulphuric acid respectively. After the removal of the above gases, hydrogen and saturated hydrocarbons were estimated by oxidation with cupper oxide at 300°C. and 600°C. The saturated hydrocarbons consisted of ethane and methane.

(1) **Experiments on the Effects of Dispersity of Catalysts.** Mixtures of one volume of acetylene and nearly two volumes of hydrogen were passed over nickel-kieselguhr catalysts at the rate of flow 5 litres per hour. Mixtures of nearly equal volumes of acetylene and hydrogen were passed over palladium-kieselguhr catalysts at the rate of flow 7 litres per hour. The composition of the resulting gases greatly depends on the dispersity of catalysts on kieselguhr. In the presence of the catalysts of small dispersity, the hydrogenation proceeds to ethane and the production of ethylene decreases. Table 1 gives the results of the experiments.

Excess of hydrogen in the reacting gases favours the production of ethane and the tendency is remarkable in presence of the catalysts of small dispersity. Table 2 gives the results of the experiments.

(2) **Experiments on the Production of Ethylene.** The effects of variation in the composition of reacting gases, reaction temperature, the rate of flow, and the addition of steam to the gases in the hydrogenation, were observed in presence of palladium-kieselguhr catalysts. From the estimation of the volumes and the composition of the gases before and after the hydrogenation, the yields of the products were calculated. Tables 3 and 4 give the results. Table 5 gives the results of the experiments with palladium distributed on the purified kieselguhr and anhydrous silicic acid.

Author's thanks are due to Prof. Dr. Bennosuke Kubota for his helpful advice and his kindly interest in the progress of this research.

(1) Treadwell und Tauber, *Helv. Chim. Acta*, **2** (1919), 601.

(2) Fujio and Shirai, *Kaigun Nenryōshō Jikkenhōkoku* (*Experimental Reports of the Japanese Naval Institute of Fuel.*), **4**, No. 4, 47.

Table 1.
Nickel-kieselguhr Catalysts

Parts of kieselguhr added to one part of nickel	Reaction temperature	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	H ₂ *	CH ₄	C ₂ H ₆	N ₂
0	100°	.0	.0	.9	34.8	57.9		6.4
20	100°	.0	5.1	1.1	43.9	41.5		8.4
100	100°	.0	15.8	.6	63.5	2.8	6.8	11.3
200	150°	.4	16.8	1.2	64.8	3.6	.8	12.2
500	200°	.9	12.6	1.1	70.8	2.8	.0	13.8

* Hydrogen was found in abundance, because acetylene underwent the polymerisation into liquid hydrocarbons.

Palladium-kieselguhr Catalysts

Parts of kieselguhr added to one part of palladium	Reaction temperature	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	H ₂	C ₂ H ₆	N ₂
50	110°	3.8	67.3	.9	1.3	22.5	4.1
150	120°	2.7	79.5	.7	1.4	9.1	6.1
500	120°	1.2	91.3	.4	1.2	2.4	4.4
800	180°	2.2	88.4	.3	.2	1.7	7.1
1500	170°	2.3	90.2	.5	1.3	1.8	4.1

Palladium-kieselguhr Catalysts

Parts of kieselguhr added to one part of palladium	Reaction temperature	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	H ₂	C ₂ H ₆	N ₂	
500	150°	1.8	90.7	.5	.0	2.6	4.4	Excess of acetylene
500	180°	2.2	91.4	.5	.0	1.1	4.8	Excess of acetylene
500	150°	1.0	83.2	.8	2.3	7.2	5.4	Excess of hydrogen
1500	200°	2.4	90.8	.2	.3	1.5	4.8	Excess of acetylene
1500	200°	1.3	84.7	.3	6.6	2.5	4.6	Excess of hydrogen
1500	150°	2.4	86.3	.8	3.1	2.6	4.8	Excess of hydrogen

Table 2.

Palladium-kieselguhr Catalysts (500 parts of kieselguhr
added to one part of palladium)

Reaction tempera- ture	Rate of flow l./hr.		Volumes c.c.	C ₂ H ₂	C ₂ H ₄	Heavy hydro- carbon	H ₂	C ₂ H ₆	N ₂	Others*	
170°	6.0	Original	1600	47.8	—	—	49.4	—	2.7		
		Product	680	1.1	89.1	.3	.0	4.4	5.1		
		% of C ₂ H ₂ converted to		1.0	79.3	—	—	3.9	—	15.8	
170°	6.0	Original	1800	50.5	—	—	47.3	—	2.2		
		Product	770	3.3	90.7	.4	.0	1.7	3.9		
		% of C ₂ H ₂ converted to		2.8	76.8	—	—	1.4	—	19.0	
180°	6.5	Original	1700	39.2	—	—	57.8	—	3.0		
		Product	810	2.3	50.1	1.2	27.1	11.5	5.6		
		% of C ₂ H ₂ converted to		2.8	61.0	—	—	14.0	—	22.2	Excess of hydrogen
170°	6.0	Original	1300	48.5	—	—	48.9	—	2.4		
		Product	570	2.4	90.4	.4	.0	1.6	5.4		
		% of C ₂ H ₂ converted to		2.2	81.0	—	—	1.4	—	14.8	Addition of steam
185°	6.5	Original	1700	49.1	—	—	48.3	—	2.6		
		Product	710	.8	90.3	.4	1.9	2.7	4.9		
		% of C ₂ H ₂ converted to		.7	76.7	—	—	2.3	—	20.3	Addition of steam
185°	6.0	Original	1700	49.6	—	—	48.3	—	2.1		
		Product	680	2.3	88.0	.5	1.6	2.1	5.4		
		% of C ₂ H ₂ converted to		1.9	71.1	—	—	1.7	—	25.3	
180°	13.0	Original	1800	47.7	—	—	50.7	—	2.4		
		Product	750	2.7	80.5	.8	8.7	2.7	4.6		
		% of C ₂ H ₂ converted to		2.4	70.3	—	—	2.4	—	24.9	
150°	7.0	Original	1600	38.5	—	—	59.2	—	2.3		
		Product	630	2.7	53.3	.8	32.7	5.5	4.9		
		% of C ₂ H ₂ converted to		3.6	70.1	—	—	7.2	—	19.1	Excess of hydrogen
185°	6.0	Original	1700	50.1	—	—	47.9	—	2.0		
		Product	680	2.1	88.8	.7	1.7	1.7	5.0		
		% of C ₂ H ₂ converted to		1.7	71.0	—	—	1.4	—	25.9	Addition of steam

Table 2.—(Concluded)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	H ₂	C ₂ H ₆	N ₂	Others	
130°	7.2	Original	1800	48.0	—	—	49.9	—	2.1		
		Product	720	2.3	86.8	.4	.8	3.5	6.2		U-glass tube used as catalyst tube
		% of C ₂ H ₂ converted to		1.9	72.3	—	—	2.9	—	22.9	
135°	12.3	Original	1800	49.7	—	—	47.6	—	2.7		U-glass tube used as catalyst tube
		Product	760	4.1	83.7	.6	5.5	1.6	4.4		U-glass tube used as catalyst tube
		% of C ₂ H ₂ converted to		3.5	71.0	—	—	1.4	—	24.1	
100°	3.7	Original	1500	50.3	—	—	47.5	—	2.2		U-glass tube used as catalyst tube
		Product	600	4.6	81.5	1.0	4.7	3.2	4.9		U-glass tube used as catalyst tube
		% of C ₂ H ₂ converted to		3.7	65.8	—	—	2.6	—	27.9	
110°	3.9	Original	1800	47.6	—	—	49.2	—	3.2		
		Product	760	3.3	81.1	1.2	.6	6.0	7.8		
		% of C ₂ H ₂ converted to		2.9	71.8	—	—	5.3	—	20.0	

* Hydrogenation was accompanied by the polymerisation of acetylene to liquid hydrocarbons. The figures were determined by difference.

Table 3.

Palladium-kieselguhr Catalysts (1500 parts of kieselguhr added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	H ₂	C ₂ H ₆	N ₂	Others	
190°	6.5	Original	1800	45.7	—	—	50.2	—	4.1		
		Product	800	2.9	78.3	.5	8.8	2.7	6.7		
		% of C ₂ H ₂ converted to		2.8	76.1	—	—	2.6	—	18.5	
200°	7.0	Original	1400	37.5	—	—	60.4	—	2.1		Excess of hydrogen
		Product	780	1.4	49.1	.7	42.4	2.1	4.3		
		% of C ₂ H ₂ converted to		2.1	73.0	—	—	3.1	—	21.8	

Table 3.—(Concluded)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	N ₂	C ₂ H ₆	H ₂	Others	
200°	9.3	Original	1700	38.0	—	—	60.0	—	2.0		
		Product	940	1.8	52.5	.8	38.2	2.2	4.5		Excess of hydrogen
		% of C ₂ H ₂ converted to		2.6	76.4	—	—	3.2	—	17.8	
200°	11.5	Original	1600	37.9	—	—	59.1	—	3.0		
		Product	880	2.1	55.5	.8	32.0	3.9	5.7		Excess of hydrogen
		% of C ₂ H ₂ converted to		3.0	80.5	—	—	5.7	—	10.8	
200°	6.0	Original	1700	50.2	—	—	47.5	—	2.2		
		Product	700	2.2	86.9	.5	3.4	1.7	5.1		Addition of steam
		% of C ₂ H ₂ converted to		1.8	71.2	—	—	1.4	—	25.6	
190°	5.5	Original	1700	49.0	—	—	47.9	—	2.1		
		Product	690	3.0	85.7	.9	4.3	1.6	4.5		Addition of steam
		% of C ₂ H ₂ converted to		2.5	71.0	—	—	1.3	—	25.2	

Table 4.

Palladium-kieselguhr Catalysts (500 parts of purified kieselguhr added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	H ₂	C ₂ H ₆	N ₂	Others
170°	7.0	Original	1800	49.3	—	—	48.8	—	1.9	
		Product	800	5.9	83.4	.7	3.6	2.7	4.6	
		% of C ₂ H ₂ converted to		5.3	75.1	—	—	2.4	—	17.2
150°	5.0	Original	1700	49.0	—	—	48.0	—	2.0	
		Product	730	2.3	87.8	.7	1.3	3.7	5.3	
		% of C ₂ H ₂ converted to		2.0	76.8	—	—	3.2	—	18.0
170°	6.2	Original	1700	37.1	—	—	59.9	—	3.0	
		Product	900	2.0	47.2	1.3	30.3	12.7	6.5	
		% of C ₂ H ₂ converted to		2.9	67.3	—	—	18.1	—	21.7

Table 5.

Palladium-anhydrous silicic acid Catalysts (500 parts of anhydrous silicic acid added to one part of palladium)

Reaction temperature	Rate of flow l./hr.		Volumes c.c.	C ₂ H ₂	C ₂ H ₄	Heavy hydrocarbons	H ₂	C ₂ H ₆	N ₂	Others
150°	4.8	Original	1800	49.9	—	—	47.9	—	2.2	
		Product	740	4.0	88.1	.6	.0	4.2	3.1	
		% of C ₂ H ₂ converted to		3.3	72.6	—	—	3.4	—	20.7
170°	9.0	Original	1800	49.2	—	—	48.7	—	2.1	
		Product	750	2.6	88.3	.8	.2	3.6	4.5	
		% of C ₂ H ₂ converted to		2.2	74.8	—	—	3.1	—	19.9

Summary.

1. In the study of the hydrogenation of acetylene in presence of nickel and palladium catalysts distributed on kieselguhr, it was observed that markedly selective action of catalysts was produced by the variation of the dispersity of the catalytic agents on kieselguhr. The phenomenon which was met with, suggests a possible mechanism of one case of promoter and carrier actions and on the other hand, a method of hydrogenation of acetylene to ethylene.

2. With regard to the simple hydrogenation process, in presence of a metallic catalyst, inert irreducible oxides being employed as the promoter and as the carrier, stimulation and restriction of the catalytic activity can be explained on the basis of the assumed co-activation of active centres on the catalytic surface by the heat of reaction.

3. Acetylene was readily hydrogenated to ethylene by the employment of the palladium-kieselguhr catalysts of proper dispersity. With equal volumes of acetylene and hydrogen, the product containing more than 90 per cent. ethylene, was obtained.

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

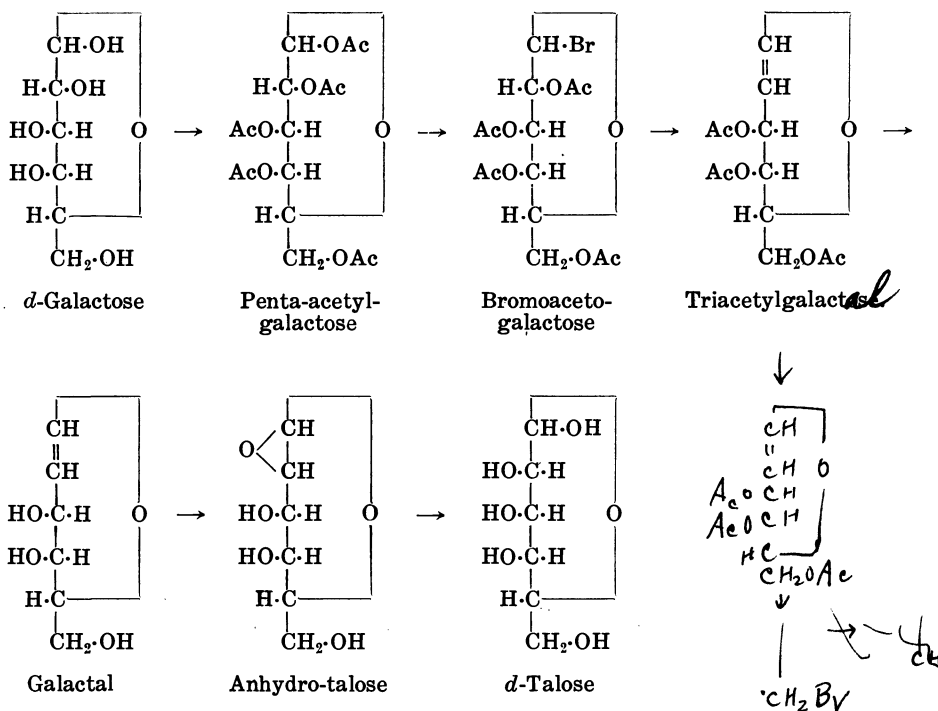
SYNTHESIS OF *d*-TALOSE FROM *d*-GALACTOSE.

By Tsutomu KOMADA.

Received May 16th, 1932. Published June 28th, 1932.

Whilst the research reported in this paper was in progress, Levene and his collaborator⁽¹⁾ published the results of an investigation of the same subject. Accordingly, the results already obtained, though somewhat imperfect, are published in their present form.

It has been shown by Bergmann and Schotte⁽²⁾ that *d*-glucose is converted into *d*-mannose by the action of perbenzoic acid on the glucal derived from the former. By a similar method, the present author prepared *d*-talose from *d*-galactose through galactal as shown in the following scheme:


 (1) *J. Biol. Chem.*, **93** (1931), 631.

 (2) *Ber.*, **54** (1921), 440.

Experimental.

Preparation of Penta-acetylgalactose and its Conversion into Acetobromogalactose.

Penta-acetylgalactose was first prepared by Erwig and König's method⁽¹⁾ by heating *d*-galactose with freshly distilled acetic anhydride and fused sodium acetate, and the acetate was then by Fischer and Armstrong's method⁽²⁾ converted into acetobromogalactose by the action of hydrogen bromide in glacial acetic acid on it.

Preparation of Triacetylgalactal. Thirty grams of acetobromogalactose were mixed with 60 gr. of zinc dust and 300 c.c. of cold 50 per cent. aqueous acetic acid. The mixture was shaken for one hour and a half, and the zinc dust was filtered off. The colourless filtrate was diluted with water, and extracted several times with ether. The ethereal solution was washed with water, neutralised with a solution of sodium bicarbonate, and again washed with water. After being dried over anhydrous sodium sulphate, the ethereal solution was evaporated. The faint yellow viscid oil thus obtained was subjected to fractional distillation under a high vacuum of 0.3–0.4 mm., when a fraction boiling at 128.5–154°C. (principally 149–154°C.) was collected. On repeating the fractional distillation, an almost colourless syrup boiling at 128.5–140°C. (principally 138–140°C.) under 0.2–0.3 mm. passed over:

Anal.: Subst. = 3.125 mg. CO_2 = 6.107; H_2O = 1.740 mg.

Found: C = 53.30; H = 6.23 %. Calc. for $\text{C}_{12}\text{H}_{16}\text{O}_7$: C = 52.94; H = 5.88 %.

Addition of Bromine and Hydrogen. An excess of chloroform solution of bromine of known strength was added to a solution of the syrup in the same solvent and, after standing for a few minutes, potassium iodide solution and dilute sulphuric acid were added, and the liberated iodine was titrated with a N/10-sodium thiosulphate solution: 0.1120 gr. absorbed 0.0695 gr. of bromine. A solution of one gram of the syrup in absolute ether absorbed 90 c.c. of hydrogen at 0° and 760 mm. in the presence of platinum black.

$\text{C}_{12}\text{H}_{16}\text{O}_7$, with an ethylenic linking, requires 0.0660 gr. of bromine and 82 c.c. of hydrogen. From these facts, there can be little doubt that the syrup is triacetylgalactal.

(1) *Ber.*, **22** (1889), 2207.

(2) *Ber.*, **35** (1902), 837.

Preparation of Galactal from Triacetylglactal. From the analogy of glucose, the use of methyl alcoholic ammonia appears to be a suitable method of hydrolysing the acetylglactal, because triacetylglucal is readily hydrolysed by the same reagent. As, however, the yield was unsatisfactory, the present author resorted to Zemplén's method.

A solution of triacetylglactal (5 gr.) in chloroform (12.5 c.c.) was mixed with a solution of sodium (0.25 gr.) in absolute methyl alcohol (12.5 c.c.) at about -20°C ., and the additive compound was hydrolysed by ice-cold water to ethyl acetate and galactal. After being neutralised with dilute hydrochloric acid, the aqueous layer was separated from the chloroform layer, shaken with animal charcoal, and filtered. The filtrate was evaporated to complete dryness under diminished pressure, when a colourless syrup was obtained. This syrup was freed from sodium chloride by dissolving it in cold absolute alcohol and filtering off any insoluble matter. In order to remove the last traces of sodium chloride, the operation was repeated several times. The syrup thus purified was still further purified by repeatedly dissolving it in cold absolute alcohol and precipitating it with absolute ether, when colourless needles were obtained in an almost quantitative yield, which melted at $95-100^{\circ}\text{C}$. with somewhat decomposition. The galactal thus obtained was to some extent hygroscopic, and still contained the traces of ash, which were very difficult to remove by recrystallisation. It readily decolorises bromine in a chloroform solution. For the next preparation, it was used without further purification.

Preparation of *d*-Talose from Galactal. For this purpose, perbenzoic acid was first prepared by a slight modification of Hibbert and Burt's method,⁽¹⁾ namely by carrying out each stage of reactions as rapidly as possible.⁽²⁾ To a solution of 10 gr. of galactal in 120 c.c. of water, a solution of perbenzoic acid (12.6 gr.) in chloroform (70 c.c.) was added, and the mixture was cooled to about 0°C ., stirred vigorously for an hour and left overnight in ice-cold water. The aqueous layer was separated from the chloroform layer, washed several times with ethyl acetate, and evaporated to a small bulk under diminished pressure.

An aliquot portion was treated with an excess of phenylhydrazine and warmed on a water-bath, when yellow crystals, melting at $184-185^{\circ}\text{C}$., were obtained, which were identified as galactosazone by the mixed melting point method.

(1) *J. Amer. Chem. Soc.*, **47** (1925), 2240.

(2) When a chloroform solution of perbenzoic acid was kept in a dark place without being previously dried, no appreciable change was observed in the concentration, even after standing for one month and a half.

The remainder was evaporated to a syrupy consistency and a solution of 1.3 gr. of the syrup in 0.5 c.c. of water was then mixed with 0.78 gr. of phenylhydrazine. After standing for three hours, the pale yellow crystals were collected, washed with ether, and purified by dissolving them in absolute alcohol, and precipitating them with absolute ether. After being washed with ether, and dried over a vacuum desiccator, they melted with decomposition at 150–178°C. As the melting points of talose and galactose phenylhydrazones are 178°C. and 160–161°C., respectively, the product consisted presumably of a mixture of *d*-talose and *d*-galactose phenylhydrazones.

Preparation of the α -Methylphenylhydrazone. A solution of the syrup (1 gr.) in water (5 c.c.) was mixed with an absolute alcoholic solution of α -methylphenylhydrazine (0.9 gr.) and the mixture was warmed on a water-bath for a short time, when colourless needles were obtained, which were collected after standing for three hours. After being successfully washed with alcohol and with ether, the crystals (m.p. 160–164°C.) were recrystallised from 30 per cent. methyl alcohol, from which they separated in colourless crystals, melting at 181.5–182°C. A mixed melting point determination with an authentic galactose- α -methylphenylhydrazone (m.p. 189–190°C.) gave m.p. 176–177°C.

From these facts, it appears that the syrup consisted of galactose and talose.

For the isolation of talose, the syrup was treated as follows: Five grams of the syrup were dissolved in water (25 c.c.) and an absolute alcoholic solution of the calculated quantity of α -methylphenylhydrazine was mixed. The mixture was allowed to stand overnight in the dark, when colourless needles of α -methylphenylhydrazone separated, which were collected, washed with absolute alcohol, and dried in a vacuum desiccator. The crystals (I) have a melting point of 165–166°C. This was recrystallised from 30 per cent. methyl alcohol, from which it separated in the crystals (II) melting at 177–178°C. Crystals (II) were again recrystallised from 30 per cent. methyl alcohol, from which they separated in colourless crystals (III) melting at 181–181.5°C. The yield was 2 gr. The mother liquor from crystals (I) was concentrated to a small bulk on a water-bath, when the crystals (IV) separated, which, after being diluted with water, were collected. The crystals were washed with the least possible quantity of absolute alcohol and ether, and then dried in a vacuum, when they melted at 152–153°C. The crystals were recrystallised twice from 30 per cent. methyl alcohol, from which they separated in the crystals (V) melting at 153–153.5°C.

Talose- α -methylphenylhydrazone was thus separated from galactose- α -methylphenylhydrazone by taking advantage of the great solubility of the former in methyl alcohol.

Crystals (III) and (V) were analysed with the following results:—

(1) Analysis of Crystals (III): 3.029 Mg. of the air-dried substance lost 0.123 mg. on heating at 105–106°C. under diminished pressure. Found: H_2O = 4.07%. Calc. for $\text{C}_{13}\text{H}_{20}\text{O}_5\text{N}_2$, H_2O : H_2O = 5.96%.

Anhydrous substance = 2.906; CO_2 = 5.809; H_2O = 1.693 mg. And subst. = 3.830 mg.; N_2 = 0.321 c.c. at 14.5°C. and 761.7 mm. Found: C = 54.52; H = 6.52; N = 9.97%. Calc. for $\text{C}_{13}\text{H}_{20}\text{O}_5\text{N}_2$: C = 54.90; H = 7.04; N = 9.86%.

(2) Analysis of Crystals (V): This substance contained no water of crystallisation. Subst. = 3.235; CO_2 = 6.516; H_2O = 2.075 mg. And subst. = 3.320 mg.; N_2 = 0.276 c.c. at 15°C. and 761.8 mm. Found: C = 54.93; H = 7.01; N = 9.88%. Calc. for $\text{C}_{13}\text{H}_{20}\text{O}_5\text{N}_2$: C = 54.90; H = 7.04; N = 9.86%.

Decomposition of the α -Methylphenylhydrazone (m.p. 181–181.5°C.) **with Benzaldehyde.** The α -methylphenylhydrazone (0.5 gr.) was mixed with a solution of benzaldehyde (0.6 gr.) in 50 per cent. alcohol (11 c.c.) and the mixture was heated on a water-bath for about two hours, when an oily product separated, which, on cooling, solidified to a pale yellow mass. After being allowed to stand overnight, it was collected, washed with alcohol and dried. The crystals thus obtained melted at 104–105°C., and this melting point was not altered on admixture with an authentic specimen of benzaldehyde- α -methylphenylhydrazone. The filtrate from the benzaldehyde- α -methylphenylhydrazone was diluted with water and most of the alcohol was removed by evaporation. After being extracted with ether, the aqueous residue was evaporated and dissolved in hot alcohol, which, on cooling, separated as colourless crystals. This was washed with 80 per cent. alcohol, when it melted at 164–165.5°C. and produced no depression of the melting point on admixture with an authentic specimen of *d*-galactose. Its specific rotation was $[\alpha]_D^{19} = +78.8^\circ$ (in water).

The Decomposition of the α -Methylphenylhydrazone (m.p. 153–153.5°C.) **with Benzaldehyde.** The decomposition of the α -methylphenylhydrazone (0.3 gr.) with a solution of benzaldehyde (0.6 gr.) in alcohol (6 c.c.) and the treatment of the filtrate from benzaldehyde- α -methylphenylhydrazone were carried out similarly as in the case of the above fraction. The aqueous solution was evaporated to a small bulk, decolorised with animal charcoal, and again evaporated to dryness, when a colourless mass was obtained, which was recrystallised from water. The specific rotation of the crystals in water was $[\alpha]_D^{17} = +14.8^\circ$.

Owing to the lack of the available substance, no determination of the melting point was made with certainty.

In conclusion, the author wishes to express his hearty thanks to Professor Hiroshi Nomura, under whose guidance this investigation was carried out.

Chemical Institute, Faculty of Science,
Tohoku Imperial University, Sendai.

NONEXISTENCE OF THE TWO MODIFICATIONS IN LIQUID NITROBENZENE AND CARBON BISULPHIDE.

By Eiji MURAKAMI.

Received May 16th, 1932. Published June 28th, 1932.

It has often been reported that some of the polar liquids undergo a sudden change in their dielectric constant in the neighbourhood of freezing point. Recently, M. Wolfke and J. Mazur, considering that it might be due to some polymorphic transformation of the liquid state and that consequently any change of other physical properties would exist, studied heating curves, dielectric constants and densities of ethyl ether, nitrobenzene and carbon bisulphide.⁽¹⁾ They concluded that a "modification change of liquid" exists at the following temperature.

Ethyl ether, -105°C .

Nitrobenzene, 9.5°C .

Carbon bisulphide, -90°C .

This year, Massy, Warren and Wolfenden⁽²⁾ have measured the density and viscosity of nitrobenzene and concluded, contrary to the opinion of Wolfke and Mazur, that there is not two modifications in liquid nitrobenzene.

Nitrobenzene.

Material. One kilogram of pure nitrobenzene from Kahlbaum ("aus kryst. Benzol") was dehydrated over calcium chloride and distilled. The part distilled at 206°C . was collected and then subjected to fractional crystallisation. The portion (100 c.c.) of highest melting point was redistilled twice under reduced pressure. The melting point of the

-
- (1) Mazur, *Nature*, **126** (1930), 649 & 993; **127** (1931), 270 & 893; **128** (1931), 673 & 761.
Wolfke and Mazur, *ibid.*, **126** (1930), 684; **127** (1931), 236, 741 & 926; **128** (1931), 584.
(2) Massy, Warren and Wolfenden, *J. Chem. Soc.*, **1932**, 91.

sample thus obtained was 5.67°C. The melting point of nitrobenzene obtained by various authors are as follows.

- 5.7° Hansen, *Z. physik. Chem.*, **48** (1904), 595.
- 5.82 Meyer, *Chemisches Zentralblatt*, **1909**, II, 1842.
- 5.70 Timmermans, *ibid.*, **1911**, I, 1669⁽¹⁾,
- 5.67 Swarts, *Rec. trav. chim. Pays-Bas*, **33** (1914), 284.
- 5.75 Turner and Polland, *J. Chem. Soc.*, **105** (1914), 1 62.
- 8.70 (?) Landolt-Börnstein, "Tabellen", 1923.
- 5.668 Roberts and Bury, *J. Chem. Soc.*, **123** (1923), 2037.
- 5.689 Sidgwick and Ewbank, *J. Chem. Soc.*, **125** (1924), 2269.
- 5.5 Mazur, *Nature*, **127** (1931), 741.
- 5.77 Massy, Warren and Wolfenden, *J. Chem. Soc.*, **1932**, 92.

It is certain that the sample used by Mazur was not quite pure. Wolfke and Mazur synthesised the nitrobenzene from benzene crystals⁽²⁾ and found its melting point to be 5.5°C. They said that the substance was thoroughly liquid at 5.7°C.⁽³⁾ Masson⁽⁴⁾ synthesised nitrobenzene from pure benzene and acids and obtained a sample freezing at 5.83°C. and found that the freezing point descends about 0.1° when exposed to air. He pointed out that the value reported by Mazur was decidedly low.

Heating Curve. Wolfke and Mazur⁽⁵⁾ found an arrest at 9.5°C. in the rate of temperature rise of nitrobenzene under constant heat supply. The same experiment was repeated by the present author to confirm their results. Some 20 c.c. of nitrobenzene was taken into a glass tube, provided with a thermometer and a stirrer, cooled to 7°C. and placed in a Dewar vessel. Dry air was incessantly passed to prevent the contamination by the moisture. The temperature of the liquid rised slowly. The thermometer was read every one minute. The temperature time curves thus obtained are shown in Fig. 1. Two curves in this figure have different inclinations showing the different heating rate. These curves, contrary to their results, are quite smooth and no arrest can be seen on any part of the curves.

Density. Mazur⁽⁶⁾ found a remarkable decrease in density of nitrobenzene between 9.5° and 5.6°C., and a sharp "Knick" in the density temperature curve at 9.5°C. For the sake of convenience, the author studied the volume change with temperature of nitrobenzene by means of a dilatometer. The capacity of the dilatometer was about 7 c.c. and

(1) See Beilsteins Handbuch der organischen Chemie, 4 Aufl. Bd. 5, Erstes Ergänzungswerk, S. 124.

(2) Wolfke and Mazur, *Nature*, **126** (1930), 993.

(3) Mazur, *ibid.*, **127** (1931), 893.

(4) Masson, *ibid.*, **128** (1931), 726.

(5) Wolfke and Mazur, *ibid.*, **127** (1931), 741.

(6) Mazur, *ibid.*, **127** (1931), 893.

the diameter of its capillary was 0.6 mm. The position of menisci of the liquid at various temperatures were read. The results are plotted in Fig. 2. As seen from Fig. 2 there is no sudden change in volume, being against to the result of Mazur.

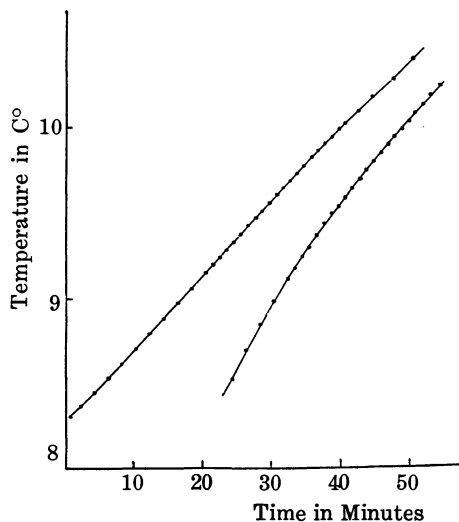


Fig. 1.

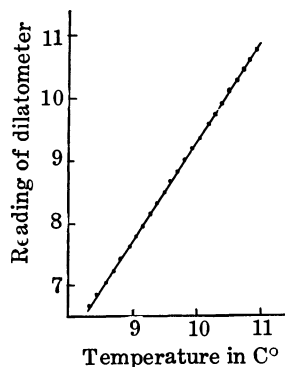


Fig. 2.

The density of nitrobenzene at 20°C. was measured by a pycnometer, and obtained the value, $d_4^{20} = 1.2030$. The value of d_4^{20} obtained by other authors are as follows.

- 1.2039 Brühl, *Z. physik. Chem.*, **16** (1895), 216.
- 1.20328 Kahlbaum, *ibid.*, **26** (1898), 646.
- 1.2028 Falk, *J. Am. Chem. Soc.*, **31** (1909), 815.
- 1.20323 Tyrer, *J. Chem. Soc.*, **105** (1914), 2538.

Refractive Index. Wolfke and Mazur⁽¹⁾ have reported, without any numerical data, that the value of the refractive index also undergoes a very distinct change at 9.6°C.

The refractive index was measured at the temperature between 7° and 20°C., especially carefully in the neighbourhood of 9.6°C., with a Pulfrich refractometer for H_α line. Owing to the construction of the refractometer it was inevitable that the sample was exposed to air, and the refractive index of nitrobenzene was found to decrease by absorbing moisture. To prevent the absorption of moisture, the liquid was protected by covering completely with rubber tubing at the upper part of the cell, as shown in Fig. 3. The vapour tension of nitrobenzene at

(1) Wolfke and Mazur, *Nature*, **128** (1931), 584.

the observation temperatures are comparatively small, so the rubber was hardly corroded, and the measurement was carried out quite satisfactorily.

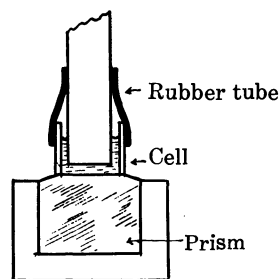


Fig. 3.

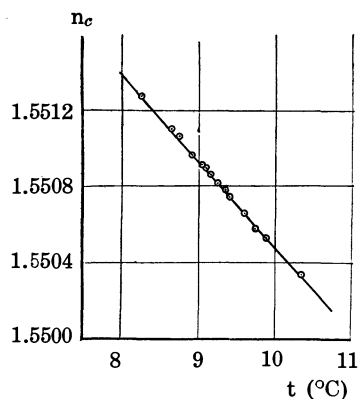


Fig. 4.

The results are given in Table 1, where n_c denotes the refractive index of nitrobenzene for H_α line. Three series of measurements have been done which indicate in Table 1 under No. 1, No. 2 and No. 3. The values of the first series are depicted in Fig. 4.

Table 1.

No. 1.		No. 2.		No. 3.	
Temp. (t)	Refractive index (n_c)	Temp. (t)	Refractive index (n_c)	Temp. (t)	Refractive index (n_c)
8.25°C.	1.55127	8.40°C	1.55118	7.45°C.	1.55167
8.60	1.55114	8.55	1.55112	8.40	1.55123
8.75	1.55106	8.65	1.55105	8.65	1.55109
8.92	1.55096	8.75	1.55102	8.90	1.55099
9.05	1.55091	9.23	1.55079	9.57	1.55079
9.10	1.55089	9.45	1.55068	9.58	1.55069
9.15	1.55086	9.55	1.55063	10.00	1.55052
9.25	1.55081	9.87	1.55050	10.30	1.55038
9.35	1.55078	9.90	1.55049	10.63	1.55025
9.42	1.55075	10.30	1.55030	11.30	1.54990
9.60	1.55066	10.45	1.55025	11.85	1.54964
9.75	1.55058	10.85	1.55006	13.30	1.54899
9.90	1.55053	10.95	1.55001	14.62	1.54837
10.35	1.55034	19.88	1.54590	16.68	1.54751
				19.30	1.54625
$n_c = 1.554992 - 0.000450t$		$n_c = 1.555037 - 0.000459t$		$n_c = 1.555060 - 0.000455t$	

The relation between refractive indices and temperatures are quite linear and no sudden change is found in any part of the line. The experimental equations calculated by the method of least squares are shown in the above table. From these three equations we obtain the following one.

$$n_d = 1.555030 - 0.000455 t.$$

Falk⁽¹⁾ obtained by measurement between 20° and 70°C. the relation:

$$n_d = 1.55453 - 0.000458 t.$$

The temperature coefficient in the Falk's equation is practically identical to that of the author.

The values of refractive index for H_α line at 20°C. obtained by various authors are as follows:

1.54593	Brühl, <i>Z. physik. Chem.</i> , 16 (1895), 216.
1.54537	Falk, loc. cit. Interpolated value.
1.54582	Brand and Kranz, <i>J. prakt. Chem.</i> , 115 (1927), 153.
1.54593	Murakami.

Carbon Bisulphide.

Wolfke and Mazur⁽²⁾ have reported that carbon bisulphide also exhibits the analogous phenomena as nitrobenzene in the heating curve at -90.03°C., and that the two modifications are discernible as they separate into two layers. The following experiment was carried out to ascertain this report.

Carbon bisulphide from Kahlbaum was purified with mercury and by distillation. The freezing point of the material was -111.0°C. The method of measurement of the heating curve was the same to that of nitrobenzene, excepting, in this case, the Dewar vessel containing a mixture of alcohol and ether was cooled with liquid air. When the carbon bisulphide was cooled down to -100°C., further cooling was stopped, and the rate of temperature rise was measured by means of a pentane thermometer. The result is shown in Fig. 5. As seen from this figure, the time temperature curve is nearly straight in the neighbourhood of -90°C.

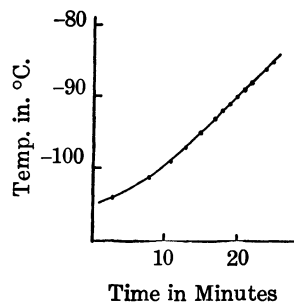


Fig. 5.

(1) Falk, loc. cit.

(2) Wolfke and Mazur, *Nature*, **127** (1931), 926.

and shows no arrest of temperature. In this case, however, as the rate of elevation of temperature is comparatively large, and the accuracy of the thermometer is not so good, the observed result may not be so accurate as the case of nitrobenzene. Moreover, two layers could not be observed anywhere between the room temperature and the freezing point.

In conclusion the author wishes to express his hearty thanks to Professor J. Sameshima for his kind guidance throughout this experiments.

Summary.

The heating rate and the volume dilatation of nitrobenzene have been measured between 8° and 11°C. and the refractive index between 7° and 20°C. The density of nitrobenzene is $d_{20}^4 = 1.2030$, and the refractive index for H_e line is given by the equation.

$$n_e = 1.555030 - 0.000455 t.$$

The heating curve of carbon bisulphide has been measured between -100° and -85°C.

No arrest in the heating curves, no distinct change of the slope in the dilatation curve and no distinct change in the value of the refractive index have been observed within the range of the observed temperatures. Two layers in liquid carbon bisulphide at -90°C. could not be observed.

None of these results proves the existence of the two modifications of the liquid nitrobenzene and carbon bisulphide such as suggested by Wolfke and Mazur.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

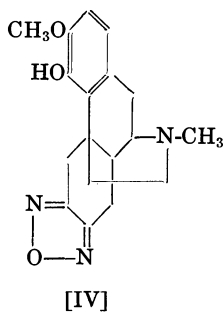
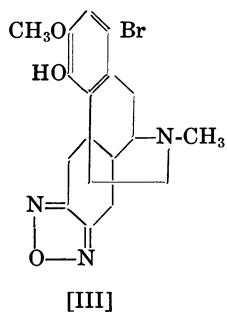
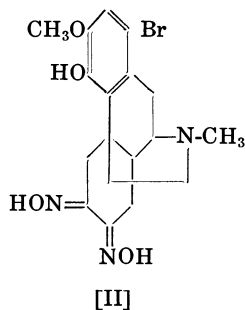
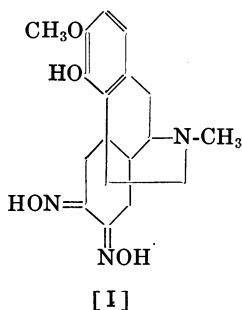
March, 1932.

**SINOMENIN UND DISINOMENIN XXXII.⁽¹⁾ ÜBER DEN
HOFMANNSCHEN ABBAU VON 1-BROM-SINOME-
NINON-DIOXIM UND DIE BROMIERUNG VON
DEN SINOMENINON-FURAZAN-DERIVATEN.**

Von Kakuji GOTO und Shingo MITSUI.

Eingegangen am 21. Mai 1932. Ausgegeben am 28. Juli 1932.

In der XXVII Mitteilung⁽²⁾ dieser Untersuchung haben wir über den Hofmannschen Abbau von Sinomeninon-dioxim⁽³⁾ [I] berichtet. Wir wollen jetzt Versuche angestellt um zu sehen ob 1-Brom-sinomeninon-dioxim [II] auch zu demselben Abbau zugänglich ist.



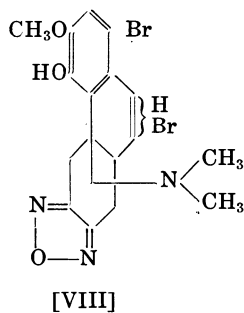
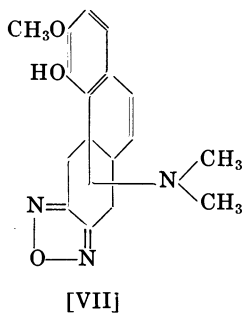
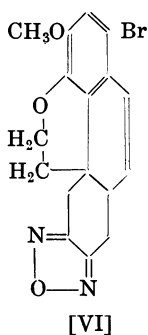
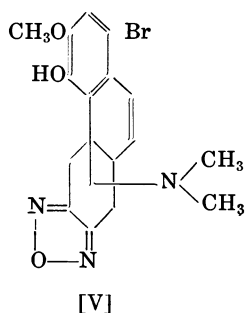
(1) XXIX Mitteilung, *Ann.*, **489** (1931), 86; XXX Mitteilung, *Ann.*, **494** (1932), 1; XXXI Mitteilung, *Ann.*, **495** (1932), 122.

(2) Diese Bulletin, **6** (1931), 197.

(3) Der dort angegebene Name Sinomeninhydrat-dioxim darf mit dieser neuen Bezeichnung ersetzt werden, da bei der weiteren Untersuchung sich ergeben hat dass das Sinomeninhydrat nichts anders als das Sinomeninon-methylalkoholat ist.

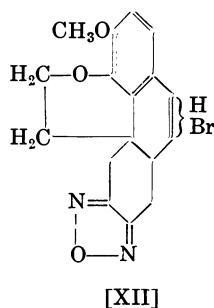
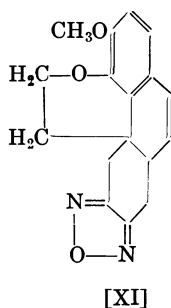
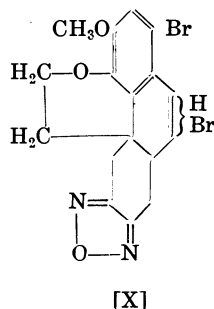
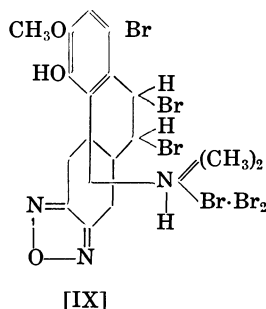
Wenn man 1-Brom-sinomeninon-dioxim mit 16.5 proc. Kalilauge einstundenlang kocht, so krystallisiert sich 1-Brom-sinomeninon-furazan [III] in schönen Prismen noch in der heissen Flüssigkeit. Die Tatsache dass in dieser Substanz wirklich ein Furazankern geschlossen ist, wird dadurch bewiesen dass Sinomeninon-furazan [IV] durch Bromierung mit ein Mol. Brom dieselbe Substanz gibt.

Das Jodmethylat von 1-Brom-sinomeninon-dioxim gibt beim Kochen mit 16.5 proc. Kalilauge des-N-Methyl-1-brom-sinomeninon-furazan [V]. Das Jodmethylat der letzteren Substanz ist nicht krystallisierend, aber wird es wieder durch Kochen mit 16.5 proc. Kalilauge ins 1-Brom-dehydro-*l*-thebenon-7-keton-furazan [VI] abgebaut.



Wie oben angeführt, gibt Sinomeninon-furazan [IV] bei der Bromierung 1-Brom-sinomeninon-furazan [III]. Aber die Bromierung von des-N-Methyl-sinomeninon-furazan [VII] gibt des-N-Methyl-1-brom-sinomeninon-furazan [V] in einer sehr schlechten Ausbeute. Hier scheint die Bromierung an der Doppelbindung C₉-C₁₀ nebeneinander sich vorzugehen. Durch Bromierung mit 2 Mol. Brom gibt dieselbe Substanz des-N-Methyl-dibrom-sinomeninon-furazan [VIII]. Von den zwei Bromatomen, muss der eine an C₁ sich befinden, sowohl aus der

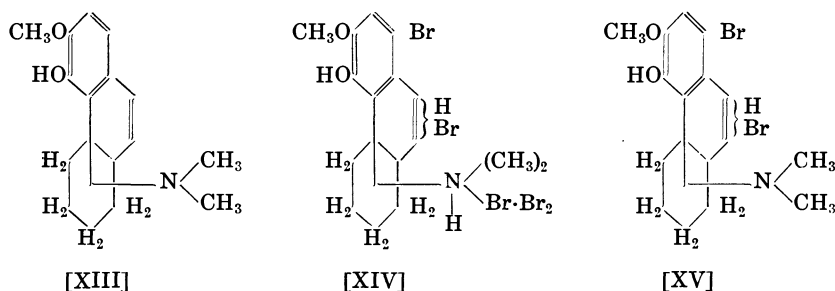
Analogie mit Sinomenin auch aus der starken Abnahme von Diazo-reaktion. Für den anderen Bromatom müssen wir die Stellung C₉ oder C₁₀ zuerteilen aus den Gründen, zu den wir später zurückkehren wollen.



Bromierung von der des-N-Methyl-substanz [VII] mit drei Mol. Brom gestaltet sich etwas anders und man gewinnt dabei ein schön krystallisierendes Perbromid [IX]. Dieser Perbromid ist beständig gegen Eisessig, aber wird er sehr leicht durch Aceton zersetzt und dabei nimmt man die Entwicklung eines zum Tränen reizenden Gases (Monobromaceton?) wahr. Dieser Perbromid enthält sechs Atome Brom und wird durch Aceton und nachfolgende Behandlung mit Ammoniak in die Dibromsubstanz [VIII] umwandelt, aber die Rückumwandlung, d.h. die Darstellung dieses Perbromides durch die Anlagerung von 1 Mol. Brom an die Substanz [VIII] ist unmöglich. Daraus folgt dass in diesem Perbromid ein Bromatom an C₁ ersetzt und zwei Bromatome sich an der Doppelbindung C₉-C₁₀ addiert haben müssen. Die äusserst grosse Krystallisationsfähigkeit dieses Perbromid scheint das Fortreissen eines Bromwasserstoffs aus C₉-C₁₀ zu verhindern. Bromierung an C₅ oder C₈ ist auch hier aus den später zu erläuternden Gründen ausgeschlossen.

Hofmannscher Abbau von dieser des-N-Methyl-dibrom-substanz [VIII] gibt einen 1,9?-Dibrom-dehydro-thebenon-7-keton-furazan [X],

welches seinerseits auch durch Bromierung von Dehydro-thebenon-7-keto-furazan [XI] mit 2 Mol. Brom sich entstehen lässt. Aber bei der Bromierung von der letzteren Substanz [XI] mit 1 Mol. Brom tritt der Brom-atom zuerst in C₉ oder C₁₀ ein, weil die resultierende Substanz [XII] ganz verschieden von dem 1-Brom-dehydro-thebenon-7-keto-furazan [VI] ist. Durch Bromierung von diesen

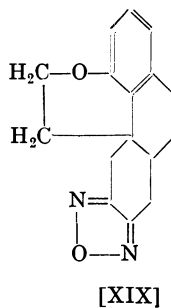
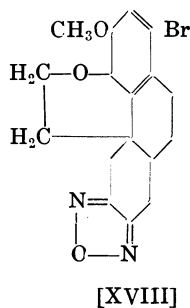
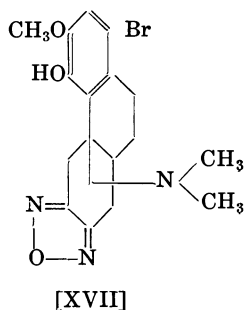
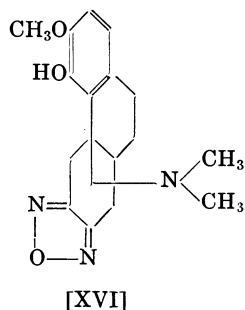


zwei verschiedene Monobrom-derivate wieder mit 1 Mol. Brom wird ein und dasselbe Dibrom-dehydro-thebenon-7-keto-furazan [X] gebildet.

In der obigen Auseinandersetzungen, ist es schwer zu bestimmen ob der zweite Bromatom an C₉ oder C₁₀ sich befindet. Das Verhältnis scheint ganz ähnlich mit dem Fall von Monobrom-phenanthren zu sein. Die Tatsache dass der zweite Bromatom sich nicht in dem hydrierten Kern des Phenanthrens befinden kann, wurde dadurch bewiesen dass das Dibrom-dehydro-*l*-thebenon-7-keto-furazan gegen Kochen mit methylalkoholischen Kali oder mit Silberacetat in Eisessig ganz beständig ist. Es ist klar dass die Bromierung an C₉ oder C₁₀ dadurch zustande kommt, indem zuerst 1 Mol. Brom sich an der Doppelbindung C₉-C₁₀ addiert und dann ein Molekül Bromwasserstoff abgespalten wird. Nur scheint in dem Perbromid von des-N-Methyl-1-brom-sinomeninon-furazandibromid [9, 10] diese Abspaltung von Bromwasserstoff verhindert werden zu sein, so lange er als solches in Krystallform sich befindet. Aber welcher von diesen zwei Brom-atomen abgespalten wird und welcher zurückbleibt, können wir zurzeit nicht bestimmen. Nur aus der Analogie mit Zimtsäuredibromid, welches bei der Behandlung mit Alkali ω -Bromstyrol gibt, sind wir geneigt anzunehmen dass der Bromatom an C₁₀ fortgerissen werden und der an C₉ zurückbleiben muss.

Um diesen Punkt und sowohl auch die Annahme genauer bestätigen dass die Furazan-gruppe, im Gegensatz zu der freien Ketongruppe, keine merkliche dirigierende Wirkung auf dem Bromatom ausübt, haben wir in der zweierlei Richtungen die Versuche angestellt. Zuerst haben wir

des-N-Methyl-demethoxy-desoxo-dihydro-sinomenin [XIII] mit 3 Mol. Brom bromiert. Dann haben wir das Perbromid von Dibrom-demethoxy-desoxo-dihydro-sinomenin [XIV] bekommen, welches merklicherweise nur fünf Atome Brom enthält. Die daraus befreite Base enthält auch nur zwei Brom-atome. So ist es klar dass das Perbromid von dieser Substanz [XIV] als solches schon ein Mol. Bromwasserstoff aus C_9-C_{10} abgespaltet haben muss. Dieser merkwürdige Unterschied zwischen den beiden Perbromiden [IX] und [XIV] muss wahrscheinlich seine Ursache in der Furazangruppe in [IX] haben. Zweitens haben wir Dihydro-des-N-methyl-sinomeninon-furazan [XVI] mit 1, 2, 3 Mol. Brom bromiert und nur ein einziges Produkt als Krystalle bekommen d.h. Dihydro-des-N-methyl-1-brom-sinomeninon-furazan [XVII]. Nur vermindert die Ausbeute nach der Menge des angewandten Broms. Daraus folgt dass das Brom hier einiger massen oxydative Wirkung ausüben kann, aber als ein einheitliches Produkt nur das 1-bromierte Substanz gibt. Die Stellung-1 wurde aus der Analogie mit 1-Brom-sinomenin und aus der sehr verminderten Diazoreaktion angenommen. Das Jodmethylat von diesem Dihydro-des-N-Methyl-1-brom-sinomeninon-furazan [XVII] schliesst sehr leicht seinen Oxydring und gibt 1-Brom-*l*-thebenon-7-keto-furazan [XVIII].



Die letzte Substanz wird auch durch Bromierung von *l*-Thebenon-7-keto-furazan [XIX] mit 1 Mol. Brom sehr leicht dargestellt.

Zusammenfassung.

Aus diesen Versuchen ergeben sich

1. 1-Brom-sinomenininon-dioxim bildet ein Furazan ebenso leicht wie Sinomenininon-dioxim.
2. Ein schwerer Atom wie Brom in der Para-stellung zu der freien Phenolgruppe verhindert nicht den Thebenon-ringschluss.
3. In Thebenon kann die Para-stellung zu der Oxido-O ebenso leicht bromiert werden, wie diejenige zur freien Phenolgruppe.⁽¹⁾
4. In Dehydro-thebenon (= 7-keto-furazan), indessen, wird zuerst die Doppelbindung bromiert und dann die Para-stellung zur Oxido-O.
5. Perbromide von zwei des-N-Methyl-basen wurden in wohl kristallisierender Form isoliert und beschrieben.

Beschreibung der Versuche.

1. **1-Brom-sinomenininon-furazan (III).** *Durch Furazan-ringschluss.* 1.0 gr. Brom-sinomenininon-dioxim (II) wird mit 10 ccm. 16.5 proc. Kalilauge einstundenlang gelinde gekocht. Schon nach fünf Minuten scheidet das Furazan in sandigen Krystallen aus. Ausbeute etwa 50 Proc. Zum Umkrystallisieren wird es in sehr verdünnter Salzsäure gelöst, dann mit konzentrierter Natronlauge kochend ausgefällt. Farblose dicke Prismen von Zers. 262°C.

Durch Bromierung. 0.5 gr. Sinomenininon-furazan (IV) wird in 10 ccm. Eisessig mit 1.5 gr. Brom (in 5 ccm. Eisessig gelöst) bei 16°C. bromiert. Nach eintägigem Stehenlassen bei der Zimmertemperatur wird die Reaktionsprodukt auf 70° ~ 90°C. bis zum vollständigen Auflösen des ausgeschiedenen Perbromids erwärmt. Man entfernt den Überschuss von Brom mit Natriumsulfit. Die daraus befreite Base wird mit Chloroform extrahiert und in der oben beschriebenen Weise gereinigt.

Mischschmelzp. zeigt keine Depression.

Subst. = 4.186 mg.; AgBr = 1.894 mg. Gef.: Br = 19.26%.

Ber. für $C_{18}H_{20}O_3N_3Br$ (406): Br = 19.68%.

2. **des-N-Methyl-1-brom-sinomenininon-furazan (V).** *Aus 1-Brom-sinomenininon-dioxim-jodmethylat.* Das Jodmethylat wird in üblicher Weise dargestellt. Zers. 254°C. (sintern 220°C.).

(1) Hierzu vergleiche auch C. Schöpf u. T. Pfeifer, *Ann.* **483** (1930), 167.

Subst. = 0.0688: AgJ = 0.0284 gr. Gef.: J = 22.31%.

Ber. für $C_{18}H_{22}O_4N_3Br$ JCH₃ (566): J = 22.44%.

Dieses Jodmethylat wird in ganz analoger Weise wie bei der Furazan-Bildung mit 16.5 Proc. Kalilauge zur des-N-Methyl-Base abgebaut. Mit Wasser und Methanol gut nachgewaschen. Ausbeute etwa 65 Proc. d. Th. Prismen vom Zers. 225°C. Halochromie mit konz. Schwefelsäure orangerot.

Durch Bromierung. Zum 0.5 gr. des-N-Methyl-sinomeninon-furazan (VII), gelöst in 10 ccm. Eisessig, setzt man 0.24 gr. Brom (1 Mol. mit 2.4 ccm. Eisessig verdünnt) bei 15°C. tröpfenweise zu. Nach üblicher Behandlung erhält man Krystallen in einer sehr schlechten Ausbeute, die sich aus dem Mischschmelzp. nichts anders als (V) erweist.

Anal.: Subst. = 6.759: CO₂ = 13.320; H₂O = 3.346 mg.

Subst. = 9.196; AgBr = 2.839 mg. Subst. = 4.534 mg.; N₂ = 0.393 ccm., 18.5°C., 755 mm.

Gef.: C = 53.74; H = 5.50; Br = 19.52; N = 9.88%.

Ber. für $C_{19}H_{22}O_3N_3Br$ (420): C = 54.03; H = 5.24; Br = 19.03; N = 10.00%.

3. des-N-Methyl-1,9?-dibrom-sinomeninon-furazan (VIII). *Durch Bromierung.* 2.0 gr. des-N-Methyl-sinomeninon-furazan VII werden in 30 ccm. Eisessig gelöst, mit 1.8 gr. Brom (etwa 2 Mol. gelöst in 18 ccm. Eisessig) bei 15°C. bromiert und übernacht stehen gelassen. Nach dem kurzen Erwärmen (10 Minuten) auf 100°C. wird der Eisessig unter vermindertem Druck abdestilliert, der ölige Rückstand in 15 ccm. Aceton aufgenommen, mit verdünntem Ammoniak (1:3) tröpfenweise versetzt und kurz erwärmt. Dabei krystallisiert das dibromierte Produkt in einer etwa theoretischen Ausbeute.

Aus Methanol gereinigt, stellt es schöne Prismen vom Zers. 212°C. (sintern 194°C.) dar. In konz. Schwefelsäure setzt, zeigt es eine orange-gelbe → gelblichbraune → braune Halochromie.

Durch Abbau des Perbromids. Die Abspaltung der perbromidartig gebundenen Brom-atomen erfolgt sich sehr leicht sowohl durch Aceton als auch durch schwefelige Säure.

(1) 2.0 gr. Perbromid (IX) werden mit 10 ccm. Aceton entweder mehrere Tage bei der Zimmertemperatur oder halbstundenlang auf 100°C. digeriert. Dabei nimmt man eine heftige Entwicklung eines lachrymatorischen Gases (Monobromaceton?) wahr. Ausbeute: 0.7 gr.

(2) 0.5 gr. Perbromid (IX) wird in 10 ccm. Wasser suspendiert, und in dieser Suspension wird ein langsamer Strom von SO₂ 10 Minutenlang eingeleitet. Da das dabei entstehende Bromhydrat von (VIII) keine Neigung zur Krystallisation zeigt, wird es in Methanol durch Ammoniak befreit und als die freie Base (VIII) erkannt. Ausbeute gut.

Anal.: Subst. = 4.117; CO_2 = 6.923; H_2O = 1.573 mg.

Subst. = 4.421; AgBr = 3.367 mg. Subst. = 3.595 mg.; N_2 = 0.261 ccm. 17°C .,
767 mm.

Gef.: C = 45.86; H = 4.25; Br = 32.41; N = 8.47%.

Ber. für $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}_3\text{Br}_2$ (490): C = 45.69; H = 4.21; Br = 32.03; N = 8.42%.

4. Perbromid von des-N-Methyl-1-brom-sinomeninon-furazan-dibromid (9, 10) (IX). Man löst 1.0 gr. des-N-Methyl-sinomeninon-furazan (VII) in 20 ccm. Eisessig und tröpft 1.5 gr. Brom (3 Mol.) in 15 ccm. Eisessig bei 15°C . etwas schnell und mit konstantem Turbinieren zu. Dann wird die Reaktionsprodukt auf 40°C . halbstundenlang erwärmt, zuletzt kurz auf 90°C . Dabei scheidet das Perbromid in prachtvollen goldgelben Säulen vom Zers. 146°C . aus. Ausbeute 70 Proc. d. Th. (1.7 gr.). Mit konz. Schwefelsäure färbt es sich blutrot $\rightarrow$ violettrot.

Anal.: Subst. = 4.778; AgBr = 6.603 mg. Subst. = 6.504 mg.; N_2 = 0.275 ccm.,
 15.5°C ., 758 mm.

Gef.: Br = 58.81; N 4.90%. Ber. für $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}_3\text{Br}_6$ (819): Br = 58.55; N = 5.16%.

5. 1-Brom-dehydro-*l*-thebenon-7-keto-furazan (VI). 0.6 gr. des-N-Methyl-1-brom-sinomeninon-furazan (V) wird durch einstündiges Kochen mit Jodmethyl in 20 ccm. Methanol in das Jodmethylat übergeführt. Da das Jodmethylat nicht krystallisierend ist, wird der ölige Rückstand wieder mit 6 ccm. 16.5 Proc. Kalilauge halbstundenlang gelinde gekocht. Allmählig geht das Öl unter Trimethylamin-Abspaltung in Krystallmassen über. Nach dem Kühlen wird es von der Kalilauge abgetrennt, mit Wasser und Methanol gut nachgewaschen.

Durch zweimaliges Lösen in heissen Eisessig und Ausfällen mit Wasser wird das Produkt analysenrein, und schmilzt bei 191°C .

Anal.: Subst. = 4.952; CO_2 = 9.903; H_2O = 1.916 mg.

Subst. = 4.372; AgBr = 2.240 mg. Subst. = 5.517 mg.; N_2 = 0.360 ccm.,
 18.5°C ., 754 mm.

Gef.: C = 54.54; H = 4.30; Br = 21.80; N = 7.43%.

Ber. für $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2\text{Br}$ (375): C = 54.40; H = 4.03; Br = 21.31; N = 7.47%.

6. 9?-Brom-dehydro-*l*-thebenon-7-keto-furazan (XII). 1.0 gr. Dehydro-*l*-thebenon-7-keto-furazan (XI) wird in 40 ccm. Eisessig heiss gelöst und bei 15°C . mit 1 Mol. Brom (0.54 gr. Brom in 5.4 ccm. Eisessig) vorsichtig bromiert.

Nach 2 stündigem Stehenlassen bei der Zimmertemperatur wird es mit viel Wasser verdünnt. Der dabei amorph ausfallende Niederschlag wird gesammelt und durch Rühren mit Aceton in Krystallen übergeführt. Farblose Tafeln. Schmelzp. $152^\circ \sim 153^\circ\text{C}$. Halochromie in konz. Schwefelsäure gelb $\rightarrow$ gelblich grün.

Anal.: Subst. = 5.185; CO_2 = 10.326; H_2O = 1.986 mg.

Subst. = 5.125; AgBr = 2.545 mg. Sust. = 4833 mg.; N_2 = 0.326 ccm. 19°C .,
760 mm.

Gef.: C = 54.31; H = 4.26; Br = 21.13; N = 7.64%.

Ber. für $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2\text{Br}$ (375): C = 54.40; H = 4.03; Br = 21.31; N = 7.47%.

7. **1, 9?-Dibrom-dehydro-l-thebenon-7-keto-furazan (X).** Diese Substanz wird in vier verschiedenen Wegen dargestellt.

a. Durch Bromierung von Dehydro-l-thebenon-7-keto-furazan (XI) mit 2 Mol. Brom. 1.0 gr. Substanz wird in 30 ccm. Eisessig heiss gelöst und bei der Zimmertemperatur dreistundenlang stehen gelassen. Man verdünnt dann mit wenig Wasser, wobei 1.0 gr. von (X) in schönen Prismen auskrystallisiert. Schmelzp. $210^\circ \sim 211^\circ\text{C}$.

b. Durch Bromierung von 9?-Brom-dehydro-l-thebenon-7-keto-furazan (XII) mit 1 Mol. Brom. 0.4 gr. Substanz wird in 10 ccm. Eisessig mit 0.17 gr. Brom (zehnfach verdünnt mit Eisessig) in üblicher Weise bromiert. Schon beim halbstündigen Stehenlassen bildet schöne Krystallen von (X). Ausbeute 0.4 gr.

c. Durch Bromierung von 1-Brom-dehydro-l-thebenon-7-keto-furazan (VI) mit 1 Mol. Brom. 0.9 gr. Substanz, gelöst in 30 ccm. Eisessig, wird mit 0.4 gr. Brom bei 15°C . vorsichtig bromiert. Nach zwei Stunden wird auf 100°C . zehn Minuten erhitzt. Beim Verdünnen mit wenig Wasser erhält man 1.0 gr. schön krystallisierte Substanz (X).

d. Durch Ether-Ringschluss von des-N-Methyl-1, 9? dibrom-sinomeninon-furazan (VIII). 0.3 gr. Substanz (VIII) wird durch ein-stündiges Kochen mit Methyljodid und Methanol ins Jodmethylat übergeführt. Das Jodmethylat ist aber nicht krystallisiert, deshalb hat man den ölige Rückstand direkt mit zehnfachen Menge von 16.5 Proc. Kalilauge abgebaut. Die Krystallen werden gesammelt, aus Eisessig und Wasser umkrystallisiert und identifiziert.

Anal.: Subst. = 5.490; CO_2 = 9.059; H_2O = 1.751 mg.

Subst. = 3.804; AgBr = 3.189 mg. Subst. = 5.841 mg.; N_2 = 0.318 ccm.,
 18.5°C ., 757 mm.

Gef.: C = 45.02; H = 3.54; Br = 35.68; N = 6.21%.

Ber. für $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2\text{Br}_2$ (454): C = 44.93; H = 3.11; Br = 35.21; N = 6.17%.

Beim Kochen dieser Substanz mit Silberacetat in Eisessig oder methylalkoholischem Kali erhält man die unveränderte Substanz quantitativ zurück.

8. **Dihydro-des-N-methyl-1-Brom-sinomeninon-furazan (XVI).** 1.5 gr. Dihydro-des-N-methyl-sinomeninon-furazan werden in 15 ccm. Eisessig mit der berechneten Menge Brom (1 Mol., zehnfach verdünnt mit

Eisessig) bei 16°C. bromiert. Beim Abdestillieren von Eisessig krystallisiert das Hydrobromid schon aus. Es wird mit Aceton gewaschen und aus heissem Wasser umkrystallisiert. Lange Nadeln. Schmp. 259°C. (u. Z.). Ausbeute sehr gut.

Subst. = 3.822; AgBr = 2.813 mg. Gef.: Br = 31.06%.

Ber. für $C_{19}H_{25}O_3N_3Br_2$ (503): Br = 31.87%.

Die freie Base wird daraus mit Soda oder Ammoniak angefällt und aus Aceton umkrystallisiert. Prismen vom Zers. 221°~223°C. (sintern 207°C.).

Anal.: Subst. = 4.408; CO_2 = 8.759; H_2O = 2.258 mg.

Subst. = 3.606; AgBr = 1.664 mg. Subst. = 4.994 mg.; N_2 = 0.410 ccm.,
16°C., 760 mm.

Gef.: C = 54.19; H = 5.69; Br = 19.64; N = 9.53%.

Ber. für $C_{19}H_{24}O_3N_3Br$ (422): C = 54.03; H = 5.69; Br = 18.96; N = 9.95%.

9. **1-Brom-*l*-thebenon-7-keto-furazan (XVIII).** (a) *Durch Ringschluss.* 0.7 gr. Dihydro-des-N-Methyl-1-brom-sinomeninon-furazan-jodmethylat wird mit 9 ccm. 16.5 Proc. Kalilauge gelinde gekocht. Unter Entwicklung von Trimethyl-amin-geruch umwendelt sich das schwimmende Oel in Krystall in fünf Minuten. Nach halber Stunde werden die Krystalle gesammelt, in Eisessig gelöst und mit Wasser gefällt. Beim schwachen Erwärmen geht der flockige Niederschlag schnell in Krystallen. Ausbeute sehr gut. Schmp. 202°~203°C.

(b) *Durch Bromierung.* 0.7 gr. *l*-Thebenon-7-keto-furazan in 7 ccm. Eisessig gelöst, wird mit 0.37 gr. Br. (1 Mol.; in 3.7 ccm. Eisessig) bei Zimmertemperatur bromiert. Beim Stehenlassen krystallisiert das Produkt in Prismen aus. Ausbeute etwa 70 Proc. Schmp. 202°~203°C. (auch die Mischprobe).

Die Substanz ist schwerer löslich in Methanol, Alkohol und Eisessig als das nicht bromierte Substanz. Es gibt keine Halochromie in Schwefelsäure.

Anal.: Subst. = 6.116; CO_2 = 12.173; H_2O = 2.476 mg.

Subst. = 5.518; AgBr = 2.755 mg. Subst. = 3.663 mg.; N_2 = 0.235 ccm.,
13°C., 760 mm.

Gef.: C = 54.28; H = 4.50; Br = 21.25; N = 7.55%.

Ber. für $C_{17}H_{17}O_3N_2Br$ (377): C = 54.09; H = 4.51; Br = 21.22; N = 7.43%.

10. **Perbromid von des-N-Methyl-1, 9?-dibrom-demethoxy-desoxydihydro-sinomenin (XIV).** 0.4 gr. Substanz (XIII) wird mit 3 Mol. Brom in ganz analoger Weise wie bei der Darstellung von Furazan-Perbromid (IX) bromiert. Ausbeute 0.7 gr. Aus heissem Eisessig umkrystal-

lisiert, stellt die Substanz schöne goldgelbe Säulen dar. Zers. 112° $\sim 113^{\circ}\text{C}$.

Halochromie in konz. Schwefelsäure blutrot $\rightarrow$ violettrot $\rightarrow$ dunkelbraun $\rightarrow$ schmutzig grün $\rightarrow$ violett.

Subst. = 4.116; AgBr = 5.507 mg. Subst. = 7.785 mg.; N_2 = 0.132 ccm., 19°C .,
760 mm.

Gef.: Br = 56.94; N = 1.94%.

Ber. für $\text{C}_{19}\text{H}_{26}\text{O}_2\text{NBr}_5$ (700): Br = 57.06; N = 2.00%.

11. des-N-Methyl-1, 9?-dibrom-demethoxy-desoxo-dihydro-sinomenin (XV). 0.4 gr. Perbromid (XIV) wird mit 10 ccm. Aceton halbstundenlang auf 100°C . erhitzt und dann mit verdünntem Ammoniak ausgefällt. Ausbeute 0.2 gr. Aus heissem Methanol umkrystallisiert. Prachtvolle Säuren von Zers. 205°C .

Anal.: Subst. = 3.731; CO_2 = 6.858; H_2O = 1.817 mg.

Subst. = 3.573; AgBr = 2.909 mg. Subst. = 2.826 mg.; N_2 = 0.072 ccm.,
 15°C ., 760 mm.

Gef.: C = 50.13; H = 5.41; Br = 34.68; N = 2.97%.

Ber. für $\text{C}_{19}\text{H}_{35}\text{O}_2\text{NBr}_2$ (459): C = 49.45; H = 5.45; Br = 34.86; N = 3.05%.

Das Chemische Laboratorium des Kitasato-Institutes,
Shiba-ku, Shirokane, Tokyo.

AN EFFECT OF POTASSIUM CYANIDE ON THE OXIDATION-REDUCTION POTENTIAL.

By Kosaku MASAKI and Takuo IKKATAI.

Received May 3rd, 1932. Published July 28th, 1932.

On the oxidation-reduction potential of the ferri-ferro complex cyanide solution many researches have been carried out and reported.

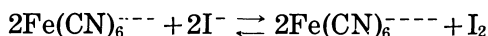
The first one who determined the potential was Fredenhagen⁽¹⁾ and in his experiment the ratio of ferricyanide to ferrocyanide was varied. Schaum and Linde,⁽²⁾ using potassium ferricyanide and sodium ferrocyanide, obtained the following formula as the result of their experiment.

(1) *Z. anorg. Chem.*, **29** (1902), 396.

(2) *Z. Elektrochem.*, **9** (1903), 407.

$$E = E_0 + 0.0002T \log \frac{(\text{total Ferricyanide})}{(\text{total Ferrocyanide})}$$

In their experiment the total concentration of complex cyanide was constant, the ratio only being changed. The addition of some electrolytes displays a powerful influence on the potentials of oxidation-reduction. In acidic solution, potassium ferrocyanide acts as an oxidizing agent and therefore we can determine the concentration of the salt with hydrogen iodide. While in neutral potassium ferrocyanide plays a reducing action to convert iodine to iodide, as follows.



Schoch⁽¹⁾ measured the potential in the presence of 0.05 molal hydrochloric acid, varying the ratio of ferricyanide to ferrocyanide. Lewis and Sargent⁽²⁾ showed that the presence of potassium ion added as potassium chloride had a large influence to lift the oxidation potential and explained this result that the added potassium ions decrease the concentration of ferrocyanide ions. Müller⁽³⁾ found that the relation between the potential and the concentration of potassium ion using potassium hydroxide is as follows (at 0°C.).

$$E = E_0 + 0.0546 \log \frac{(\text{total ferricyanide})(\text{K}^+)}{(\text{total ferrocyanide})}$$

According to Schoch and Felsing⁽⁴⁾ the relation is as follows;

$$E = E_0 + 0.0591 \log \frac{(\text{Fe}(\text{CN})_6^{---})(\text{K}^+)^x}{(\text{Fe}(\text{CN})_6^{----})}$$

and the value of x varies between 0.725 and 0.75. They obtained these relation using potassium chloride at 25°C. Linhart⁽⁵⁾ also investigated the influence of potassium chloride in the similar manner.

Moreover, on the influence of hydrogen ion, Müller and Kolthoff⁽⁶⁾ reported their results. The former obtained the following equation at 18°C.,

$$E = E_0 - 0.546 \log (\text{H}^+)^2$$

(1) *J. Am. Chem. Soc.*, **26** (1904), 1422.

(2) *J. Am. Chem. Soc.*, **31** (1909), 355.

(3) *Z. physik. Chem.*, **88** (1914), 46.

(4) *J. Am. Chem. Soc.*, **38** (1916), 1928.

(5) *J. Am. Chem. Soc.*, **39** (1917), 615.

(6) *Z. anorg. Chem.*, **110** (1920), 143.

while the latter at the same temperature,

$$E = 0.416 - 0.0577 \log (H^+)^{2.22}$$

and in the experiments the ratio of ferricyanide to ferrocyanide was 1:1, each concentration being $\frac{1}{2}$ (0.025) mol per litre. In this investigation the influence of added potassium cyanide was measured at the various concentration of the salt.

Experimental Part.

The apparatus used is shown in the diagram. A: Hydrogen inlet; B: Thermometer; C: Platinum electrode; D: Solution inlet; E: Hydrogen outlet; F: Salt bridge (0.1 m KCl); G: Salt vessel (0.1 m KCl); H:

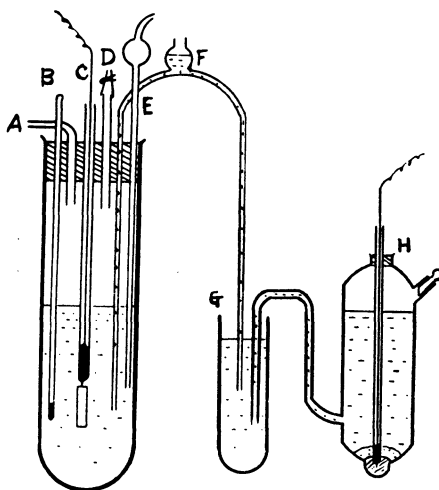
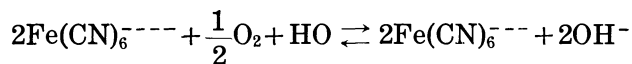


Fig. 1.

Calomel electrode. This investigation was carried out in the hydrogen atmosphere. Because in the alkaline solution, as we described above, potassium ferrocyanide behaves as a pretty powerful reducing agent in contact with air as following.



Potassium ferricyanide and ferrocyanide employed were of Kahlbaum's, and each was made into 0.05 molal solution with distilled water at the least contact of air. The potassium cyanide was also of high

purity and standardised with 0.1 normal silver nitrate solution. Potassium cyanide was added in the mixture of each 10 c.c. of the ferricyanide and ferrocyanide solution and the volume of this solution was enlarged to 50 c.c. with distilled water. Thus the ratio of ferricyanide to ferrocyanide was 1:1, and each of these concentration was 0.01 molal. The vessel was filled with hydrogen before the solution was poured into it. The hydrogen gas was prepared by using pure metallic zinc and sulphuric acid, and washed with potassium permanganate and then potassium hydroxide.

The electrode used was non-platinized platinum plate of about 1 cm. $\times$ 3 cm. The construction of the cell was as follows;



The temperature of the cell was kept constant at $30^\circ \pm 0.05^\circ \text{C}$. in a thermostat. The results are shown in the table.

$\text{K}_4\text{Fe}(\text{CN})_6$	$\text{K}_3\text{Fe}(\text{CN})_6$	KCN	E_c	E_h^*	E_h (calc.)
0.01	0.01	0	0.0684	0.4094	
0.01	0.01	0.0321	0.0747	0.4157	0.4130
0.01	0.01	0.0642	0.0798	0.4208	0.4238
0.01	0.01	0.0963	0.0855	0.4265	0.4300
0.01	0.01	0.1284	0.0892	0.4302	0.4344
0.01	0.01	0.1605	0.0920	0.4330	0.4379
0.01	0.01	0.1926	0.0953	0.4363	0.4409
0.01	0.01	0.0922	0.0872	0.4282	0.4294
0.01	0.01	0.1844	0.0950	0.4360	0.4400
0.01	0.01	0.2766	0.1040	0.4450	0.4468
0.01	0.01	0.3688	0.1113	0.4523	0.4507
0.01	0.01	0.4610	0.1165	0.4575	0.4541
0.01	0.01	0.5532	0.1182	0.4592	0.4569
0.01	0.01	0.2895	0.1052	0.4461	0.4469
0.01	0.01	0.5730	0.1194	0.4604	0.4576
0.01	0.01	0.7238	0.1220	0.4630	0.4610
0.01	0.01	0.8685	0.1242	0.4652	0.4633
0.01	0.01	1.0132	0.1252	0.4662	0.4662
0.01	0.01	1.1580	0.1257	0.4667	0.4663

* Potential of 0.1 normal KCl-calomel electrode : $0.3387 + 7.9 \times 10^{-4} (t - 25)$.

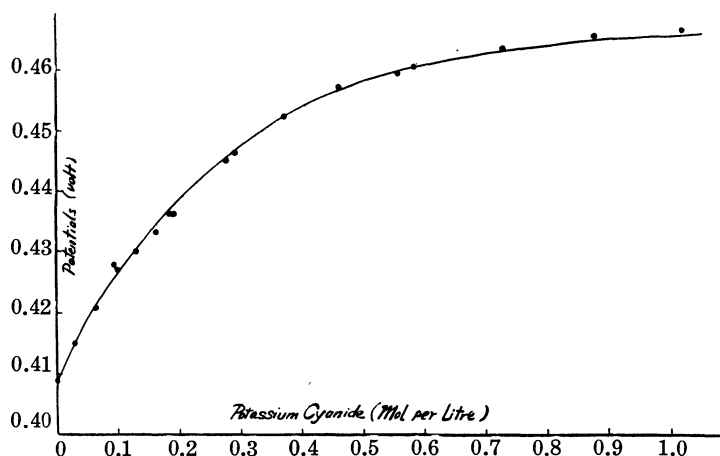
Kust Arudt, *Physikalische-chemie Technik*, (1923) 795.

Auerbach, *Z. Elektrochem.*, **18** (1912), 13.

Lewis and Brighton, Sebastian. *J. Am. Chem. Soc.*, **39** (1917), 2245.

Fales and Vasbargh, *ibid.*, **40** (1918), 291.

In the table E_c is the measured potential against a decinormal calomel electrode and E_h is the potential against a hydrogen electrode at 25°C. and Fig. 2 shows the value of E_h by the changes of concentrations of potassium cyanide.



From the data, we obtained the following approximate formula

$$E = 0.4660 + 0.0601 \log K^{0.59}$$

where K is the concentration of the potassium cyanide added. The last column in the above table shows the calculated values by this equation.

Under sunlight, we practised many investigations, but all those were worthless giving no systematic results. This is probably due to the decomposition of double cyanide by sun beams. So the author carried out this investigation in the dark room. The effect of more concentrated cyanide is more or less uncertain giving the fluctuation of potential by some disturbance.

Summary.

(1) The effect of the existence of potassium cyanide upon the oxidation-reduction potential of potassium ferricyanide and ferrocyanide was investigated.

(2) The investigation was performed in the hydrogen atmosphere in the dark room to avoid the atmospheric oxidation and the photochemical decomposition.

(3) The result can be expressed approximately by the following empirical formula at 30°C.

$$E = 0.4660 + 0.0601 \log K^{0.59}$$

where K is the concentration of potassium cyanide, and each concentration of potassium ferricyanide and potassium ferrocyanide is 0.01 mol. respectively.

Yokohama Higher Technical School,
Yokohama.

THE ACTIVITY COEFFICIENT OF ZINC SULPHATE FROM ELECTROMOTIVE FORCE MEASUREMENTS.

By Kosaku MASAKI and Takuo IKKATAI.

Received May 3rd, 1932. Published July 28th, 1932.

In the early days of the development of the activity coefficient few investigators⁽¹⁾ reported on the activity coefficient of zinc sulphate in the following cell



but the results may be uncertain by the solubility of mercurous sulphate. Recently Cowperthwaite and LaMer⁽²⁾ had the excellent investigation upon the cell



and determined the activity coefficient of zinc sulphate in the various concentrations which is in good conformity with the predictions of the Gronwall, LaMer and Sandved's⁽³⁾ extension of the Debye-Hückel theory.⁽⁴⁾

In this investigation we measured the electromotive force of the cell (1) with a more concentrated range on which Cowperthwaite and LaMer made no investigation and we calculated the activity coefficient of zinc sulphate.

(1) Lehfelddt, *Z. physik. Chem.*, **35** (1900), 257; Cohen, Chattaway and Tombrock, *Z. physik. Chem.*, **60** (1907), 706; **61** (1907), 384; **75** (1910), 1.

(2) *J. Am. Chem. Soc.*, **53** (1931), 4333.

(3) *Physik. Z.*, **29** (1928), 358.

(4) *Ibid*, **24** (1923), 185.

Theoretical.

Debye and Hückel introduced an approximate equation early in the development of their theory of strong electrolytes, solving the Poisson's equation by retaining only the linear term resulting from the expansion of the exponential in the Boltzmann's expression for the density of electricity for mathematical simplicity and they had many experimental investigations which demonstrated that the activity coefficients of strong electrolytes in aqueous solution agree fairly well with the predictions given by their equations. But even in regions of high dilution there are serious discrepancies between the calculated values from these equations and the experimental data. Gronwall, LaMer and Sandved obtained the following expression, solving the Poisson's equation by using the complete form of the Boltzmann's expression, for the activity coefficient of an electrolyte of symmetrical type, i.e. $Z_1 = -Z_2 = Z$.

$$\log f = -\frac{\epsilon^2 Z^2}{kTDa} \times \frac{1}{2} \times \frac{x}{1+x} + \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 Z^2}{kTDa} \right)^{2m+1} \left[\frac{1}{2} X_{2m+1}(x) - 2m Y_{2m+1}(x) \right]. \quad (3)$$

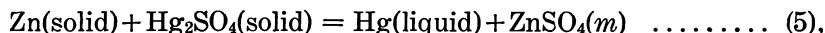
In the above equation, $x = Ka$, and $K = \sqrt{\frac{8\pi N \epsilon^2 Z^2 c}{1000 kTD}}$, D is the dielectric constant of water ($D = 78.54 [1 - 0.0046(t - 25) + 0.0000088(t - 25)^2]$)⁽¹⁾, Z is the valence of the cation and anion, ϵ is the charge of an electron ($\epsilon = 4.774 \times 10^{-10}$), k is Boltzmann's constant ($k = 1.372 \times 10^{-16}$), N is Avogadro's number ($N = 6.061 \times 10^{23}$), a is the distance of closest approach of the two ions, c is the concentration in moles per litre of solution, and $X(x)$ and $Y(x)$ are known functions of x .

Putting numerical values in (3) Gronwall, LaMer and Sandved got the following working equation

$$\begin{aligned} -\log_{10} f = & 1.53636 \left(\frac{Z^2}{a} \right) \frac{x}{1+x} - 0.15382 \left(\frac{Z^2}{a} \right)^3 \cdot 10^3 \left[\frac{1}{2} X_3(x) - 2Y_3(x) \right] \\ & - 0.0770 \left(\frac{Z^2}{a} \right)^5 \cdot 10^5 \left[\frac{1}{2} X_5(x) - 4Y_5(x) \right] \dots\dots\dots (4) \end{aligned}$$

Numerical values for the functions $10^3 [1/2 X_3(x) - 2Y_3(x)]$ and $10^5 [1/2 X_5(x) - 4Y_5(x)]$ were tabulated by the Gronwall, LeMer and Sandved for various assigned values of x . Therefore the value for these functions at any desired x may be obtained from their tables by interpolation.

The electromotive force of the cell (1), corresponding to the following process.



is given by the equation

$$\begin{aligned} E &= E_0 - \frac{RT}{2F} \ln m_{\text{Zn}^{++}} \cdot f_{\text{Zn}^{++}} - \frac{RT}{2F} \ln m_{\text{SO}_4^{--}} \cdot f_{\text{SO}_4^{--}} \\ &= E_0 - \frac{RT}{2F} \ln m_{\text{Zn}^{++}} - \frac{RT}{2F} \ln m_{\text{SO}_4^{--}} - \frac{RT}{2F} \ln f_{\text{Zn}^{++}} \cdot f_{\text{SO}_4^{--}} \\ &= E_0 - \frac{RT}{2F} \ln m_{\text{Zn}^{++}} - \frac{RT}{2F} \ln m_{\text{SO}_4^{--}} - \frac{RT}{F} \ln f_{\pm} \quad \dots\dots\dots (6) \end{aligned}$$

For 25°C., this equation (6) takes the following form

$$E = E_0 - 0.05915 \log m - 0.05915 \log f \quad \dots\dots\dots (7)$$

For convenience in plotting and calculating the mean activity coefficient $f_{\text{ZnSO}_4} = \sqrt{f_{\text{Zn}^{++}} \cdot f_{\text{SO}_4^{--}}}$, we calculate the quantity E'_0 , where

$$E'_0 = E + 0.02957 \log m + 0.02957 \log f \quad \dots\dots\dots (8)$$

$$E'_0 = E_0 - 0.05915 \log f \quad \dots\dots\dots (9)$$

and the intercept of extrapolated E'_0 at zero concentration gives the value of E_0 .

Experimental.

Preparation of Materials. Mercurous sulphate: Kahlbaum's "for analysis" was employed and kept in the dark room.

Zinc sulphate: Kahlbaum's "for analysis" was employed without recrystallization. The salt was dissolved in conductivity water and stored in a steamed-out hard glass flask equipped with a stopper which was devised to make the evaporation least possible.

Mercury: Purified mercury was washed ten times with a mixture of dilute mercurous nitrate and nitric acid and distilled thrice in a reduced pressure with a current of air.

Zinc: A purest profitable zinc stick was employed.

Zinc amalgam: The zinc stick stated above was attached to a nip of a Pt wire which was sealed into a glass tube at the end. Then the joint and Pt part was covered with highest grade sealing wax, and the zinc was amalgamated after being scraped clean from oxide.

Analysis of Zinc Sulphate Solution. Kahlbaum's zinc sulphate was dissolved in conductivity water to form a stock solution from which dilutions were made by weight. Besides, a weighed salt was dissolved in a weighed quantity of conductivity water to prove the accuracy of the analytical method employed. The determinations of the concentration was performed as described by Cowperthwaite and LaMer. A weighed sample of the solution was carefully evaporated to dryness in a steam oven and then the residue was heated in an air oven at 300°C . for several hours after treated with a small quantity of strong sulphuric acid. Then the bottle was cooled in a desiccator and weighed. Then treating with sulphuric acid, heating at 300°C . and weighing were repeated till the weight of the dried mass became constant. The residue was the weight of anhydrous zinc sulphate. This method is quite satisfactory. The reference solution which was made to be 1.03955 mol was determined by this method as 1.03967 mol. The error was only 0.02% and in a region of the experimental error. The stock solution was determined as 1.16994 mol.

Experimental Method. According to Landolt's "Physikalisch-chemische Tabellen" the system of zinc-mercury forms no compound nor solid solution and the composition of the liquid phase is definite at a given temperature when the solid phase coexists. Hence an amalgamated zinc can be employed as a reversible and reproducible zinc electrode. We made pairs of electrodes mentioned above and each of them was proved to be identical within 0.02 mv. They were kept in the nitrogen atmosphere to prevent the oxidation. But in its practical employment at the temperature 25°C . the presence of air is considered to give a little effect on it. The cells gave a constant electromotive force within two or six hours even in air. A slight scum on the surface of the cathode was found after four days.

The zinc sulphate solutions which were made by weight from the stock solution were saturated with mercurous sulphate in a thermostat maintained at $25^{\circ} + 0.05^{\circ}\text{C}$. for two days with frequent shaking. The cells used had the special form as Fig. 1. In this figure, 1: the red wax, 2: zinc amalgam. The electromotive forces of the cell were measured after being kept in the thermostat at

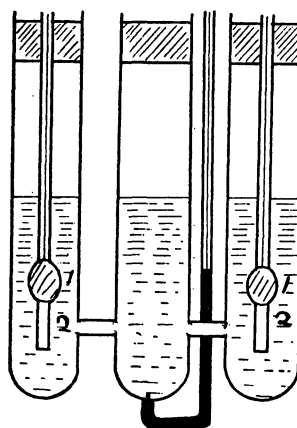


Fig. 1.

25°C. for one hour and the average values of two or three cells were described in the table.

Experimental Data. The experimental values of the electromotive force and the computed function E are given in Table 1. The observed electromotive force given in column 3 is the average value of two or three cells, each of the cell being nearly identical with a little difference of 0.05 mv. A correction for the solubility of mercurous sulphate is

Table 1.

E.M.F. of the Cell Zn-Hg(sat. amalgam) | $\text{ZnSO}_4(m)$,
 $\text{Hg}_2\text{SO}_4(s)$ | Hg at 25°C.

No.	Molality of ZnSO_4	E (obs.)	Molality of total SO_4^{--}	0.02957 $\log m \text{ Zn}^{++}$	0.02957 $\log m \text{ SO}_4^{--}$	E_0'
1	3.000	1.43048	3.000	+0.01411	+0.01411	1.45870
2	2.500	1.43646	2.500	.01177	.01177	1.46000
3	2.000	1.44375	2.000	.00391	.00391	1.46156
4	1.800	1.44648	1.800	.00755	.00755	1.46158
5	1.600	1.44803	1.600	.00604	.00604	1.46010
6	1.400	1.45094	1.400	.00432	.00432	1.45958
7	1.000	1.45595	1.000	.00000	.00000	1.45595
8	1.16994	1.45415	1.17014	.00202	.00202	1.45819
9	0.934504	1.45736	0.934676	— .00087	— .00087	1.45562
10	.699756	1.46240	.699959	.00458	.00458	1.45108
11	.465742	1.46547	.465939	.00981	.00981	1.44585
12	.387925	1.46708	.388101	.01216	.01216	1.44276
13	.232547	1.47292	.232736	.01874	.01873	1.43535
14	.165698	1.47736	.165909	.02309	.02308	1.43119
15	.128833	1.48073	.129053	.02632	.02630	1.42811
16	.105386	1.48301	.105639	.02890	.02887	1.42524
17	.0891541	1.48498	.0893737	.03104	.03101	1.42293
18	.0772633	1.48663	.0774078	.03288	.03285	1.42090
19	.0681679	1.48832	.0684336	.03449	.03444	1.41939
20	.0609883	1.48973	.0612565	.03592	.03586	1.41795
21	.0441321	1.49295	.0444176	.04008	.04001	1.41286
22	.0101087	1.51370	.0105397	0.5901	.05347	1.39622
23	.0039726	1.52326	.0045819	.07101	.06916	1.38303
24	.0020793	1.52808	.0028429	.07932	.07529	1.37347
25	.0008558	1.53310	.0018150	.09072	.08106	1.36132
26	.0004321	1.53465	.0015055	.09950	.08346	1.35169

necessary at the concentration of 0.232547 molal solution or less. This was made by calculating the increase of concentration of sulphate ion in the solution which is due to the slight solubility of the mercurous sulphate, and calculating the potential resulting therefrom.

Drucker⁽¹⁾ reported the solubility of mercurous sulphate at 25°C. to be 11.71×10^{-4} mol per litre. LaMer and Parks⁽²⁾ studied the parameter of CdSO_4 and reached to the conclusion that the value is larger than 3.6 Å but less than 3.7 Å. Also Cowperthwaite and LaMer got the value 3.64 Å for zinc sulphate. Hereupon we assumed that for mercurous sulphate the parameter $\bar{a}$ is 3.7 Å. Then by the Gronwall, LaMer and Sandved's equation we can find the activity coefficient f as 0.704. In order to calculate the increase in sulphate ion we used the equation

$$m_{\text{Hg}_2^{++}} \cdot f_{\pm} \cdot m_{\text{SO}_4^{--}} \cdot f_{\pm} = a_{\text{Hg}_2^{++}} \cdot a_{\text{SO}_4^{--}} = k = 6.80 \times 10^{-7}$$

Then an approximation was performed as

$$x(fm+x) = k \dots\dots\dots (10)$$

where x is the mean activity resulting from the mercurous sulphate dissolved, and the mean activity coefficient was calculated by (4) at concentration m . The solubility was obtained by x/f . Accurately saying, f is the mean activity coefficient at $m+f/x$, and repeated calculations are necessary for dilute solutions. The procedure is as follows.

The solubility m_1 obtained by the first calculation was added to m and f_2 was calculated at $(m+m_1)$ and x_2 was obtained by (10). This procedure was repeated to get a practically constant solubility. For instance for No. 26.

By 1st calculation	2nd	3rd	4th	5th	6th
$m_{\text{Hg}_2\text{SO}_4} = 0.000842$	0.0010276	0.0010659	0.0010720	0.0010734	0.0010734

The values of E'_0 are shown graphically in Fig. 2. The values for dilute solutions, where the solubility of mercurous sulphate amounts to some 4% or more of the total concentration, abnormally decreases with increasing dilution.

(1) *Z. anorg. Chem.*, **28** (1901), 362.

(2) *J. Am. Chem. Soc.*, **53** (1931), 2040.

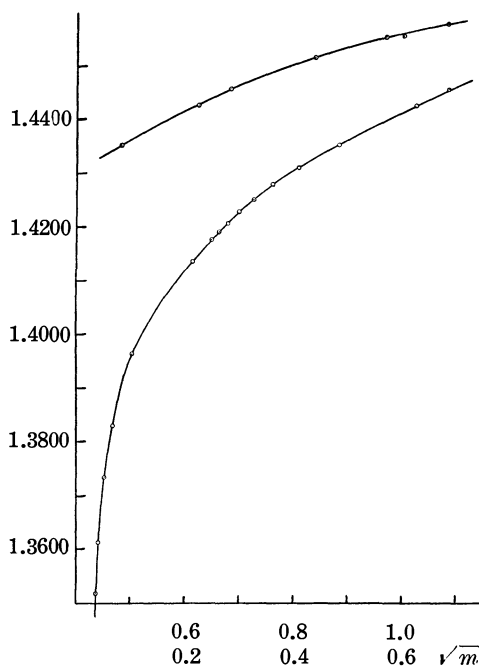


Fig. 2.

Discussion of Results. The abnormal decrease of E'_0 in highly dilute solutions prevents us from the interesting application of the Gronwall, LaMer and Sandved's extension of the Debye-Hückel's theory. Because the extension is expected to be valid in the concentration range up to 0.01 molal solution. The cause of the anomaly can be attributed to either the self discharge effect or the absurd assumption that the parameter $\bar{a}$ of mercurous sulphate is 3.7 Å. Upon these problems we will render the same discussion in a following paper. Cowperthwaite and LaMer determined the activity coefficient of zinc sulphate in dilute solution at 25°C. as follows.

Molality	0.0005	0.001	0.002	0.005	0.01	0.02	0.05
Calc.	0.780	0.701	0.608	0.478	0.386		
Obs.	0.780	0.700	0.608	0.477	0.387	0.297	0.206

We used these data for the determination of E_0 and the activity coefficient in more concentrated parts. For by the equation

$$E'_0 = E_0 - 0.05915 \log f$$

we can plot $E'_0 - E_0$ against the square root of the molality to which the activity coefficient is assigned, and the extrapolation of our data to

higher dilutions was carried out strictly parallel to the curve $E'_0 - E_0$. This is shown in Fig. 3.

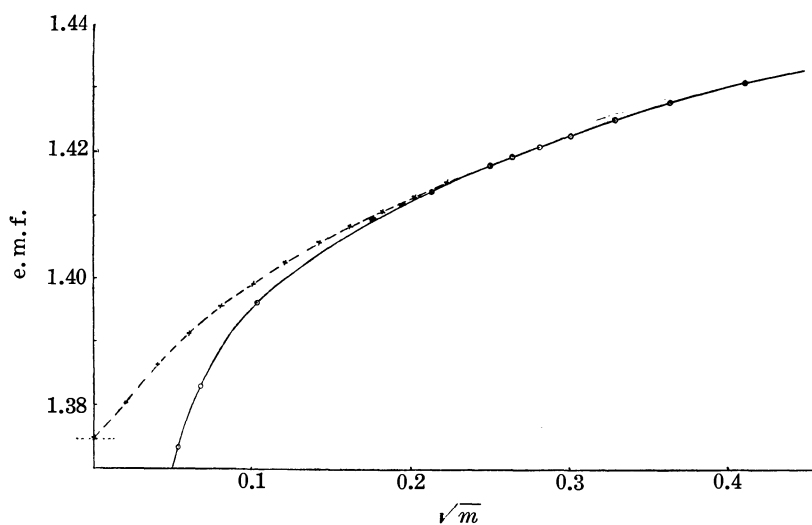


Fig. 3.

Table 2.
The Activity Coefficient of Zinc Sulphate at 25°C.

No.	Molality of total SO_4^{--}	Activity Coef. $E_0=1.37375$	$E_0=1.37470$	$E_0=1.37480$
1	3.000	0.0381		
2	2.500	0.0362		
3	2.000	0.0341		
4	1.800	0.0340		
5	1.600	0.0361		
6	1.400	0.0368		
7	1.000	0.0422		
8	1.17014	0.0389	0.0388	0.0389
9	0.934676	0.0429	0.0429	0.0430
10	0.699959	0.0493	0.0492	0.0494
11	0.465939	0.0628	0.0627	0.0629
12	0.388101	0.0708	0.0707	0.0710
13	0.232736	0.0945	0.0943	0.0947
14	0.165909	0.1111	0.1107	0.1113
15	0.129053	0.1253	0.1251	0.1255
16	0.105639	0.1401	0.1400	0.1403
17	0.0893737	0.1533	0.1530	0.1536
18	0.0774078	0.1659	0.1656	0.1662
19	0.0684336	0.1759	0.1756	0.1762
20	0.0612565	0.1860	0.1856	0.1864

We find graphically joint of the E'_0-E_0 curve and the experimental E'_0 curve where the dissolved mercurous sulphate is so little as to give no effect on the study of E_0 . Thus we find E_0 as 1.37475. The activity coefficient calculated by this value for E_0 is tabulated in Table 2. The most possible value for E_0 is 1.37475, but two slightly different values are used to the calculation of the activity coefficient. These results are given in columns 2 and 3.

Using the values measured by Cowperthwaite and LaMer, we tabulated the activity coefficient of zinc sulphate for round concentration in Table 3. The third column was compiled from the data of LaMer and Parks for cadmium sulphate at 25°C.

Table 3.
Mean Activity Coefficient for Round Concentration.

Molality	ZnSO ₄	CdSO ₄
1.000	0.0422	0.0418
0.500	0.0596	0.0605
0.200	0.101	—
0.100	0.144	0.137
0.050	—	0.199
0.010	0.387	0.383
0.005	0.477	0.476
0.002	0.608	—
0.001	0.700	0.699
0.0005	0.780	0.774

Summary.

1. Electromotive forces of the cell, Zn-Hg (sat amalgam) | ZnSO₄(*m*), Hg₂SO₄(s) | Hg, were measured at 25°C. in the range of the concentrations of 0.0004321 to 3 molál.

2. The electromotive force of higher dilutions is quite abnormal owing to the solubility of mercurous sulphate.

3. The mean activity coefficients of zinc sulphate for more concentrated parts were calculated by using the Cowperthwaite and LaMer's data about dilute solutions. The potential E_0 of the cell, when ion activities of zinc sulphate are hypothetically one molal, was found to be 1.37475 volt at 25°C.

Yokohama Higher Technical School,
Yokohama.

STUDIES ON REACTIONS BETWEEN GAS AND SOLID. IV.
AZOTATION OF CALCIUM CARBIDE AND THE
EFFECT OF TEMPERATURE ON ITS VELOCITY.⁽¹⁾

By Takeo AONO.

Received May 27th, 1932. Published July 28th, 1932.

Experimental.

Experimental Procedure. The method and apparatus of these experiments were nearly the same as those reported in the former paper.⁽²⁾ But in this case the pressure of nitrogen was kept constant (1 atm.) and the velocity of the reaction was determined by measuring the speed of absorption from time to time with a second differential manometer of bromonaphthalene attached to the reaction tube. At the end of the reaction or after a definite time the tube was rapidly cooled and the product was weighed and analysed. The content of nitrogen at a given moment was obtained by graphically integrating the $\left(-\frac{dP}{dt} \text{ or } -\frac{dm}{dt} \sim t\right)$ curve and comparing the integrated value with the final analysis.

Effect of Temperature. The effect of temperature on the reaction velocity is shown in Table 1 and Figs. 1, 2 and 3. The time was measured from the beginning of introducing nitrogen into the tube, and it took about $\frac{1}{2}$ –1 minute to reach 1 atm. From Fig. 1 we see that the velocity of absorption of nitrogen is very small at first and increases rapidly up to a maximum value and then gradually decreases. The results are similar to those obtained by H. H. Frank and his co-workers.⁽³⁾

The initial increase of the velocity is probably due to the following causes:

- (a) liberation of the heat of reaction: $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C} + 54.8\text{Cal.}$,⁽⁴⁾ which elevates the temperature of the reacting mass locally,⁽⁵⁾ the greater the reaction velocity the greater will be the temperature elevation and consequent acceleration;

(1) Read before the Chemical Society of Japan, Dec. 1931.

(2) T. Aono, *This Bulletin*, **7** (1932), 143–154.

(3) H. H. Franck, F. Hochwald and G. Hoffmann, *Z. phys. Chem.*, Bodenstein-Festband, (1931), 985.

(4) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **34** (1931), 890.

(5) The local elevation of temperature was measured and reported by G. Bredig, *Z. Elektrochem.*, **13** (1907), 69.

Table 1.

Azotation velocity of powdered carbide ($\text{CaC}_2 = 68.2$, $\text{CaF} = 1.2\%$)
at various temperatures.

Temp. °C.	867		950		1000		1060		1090		1140	
Carbide, gr.	4.0043		4.0066		4.0055		4.0068		4.0002		4.0013	
Exp. No.	361		359		362		360		363		365	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1			1.100	1.16		0.76	0.356	0.23	0.441	0.43		
2	0.256	0.40	1.116	2.44	1.242	1.93	0.664	0.75	0.619	1.00	0.346	0.40
3	.265	0.65	1.077	3.62	1.443	3.41	1.44	1.79	1.001	1.86	1.266	1.26
4	.264	0.90	1.052	4.73	1.577	5.05	2.91	4.02	2.74	3.72	3.925	4.31
5	.253	1.14	1.016	5.82	1.625	6.80	4.085	7.81	7.25	8.91	9.10	11.80
6	.231	1.37	0.983	6.87	1.613	8.55	4.63	12.56	14.93	21.43	14.29	26.15
7			0.956	7.89			4.33	17.44	14.28	27.36	13.34	44.10
8	.198	1.77	0.922	8.87	1.528	12.00	3.51	21.58	9.01	40.43	8.13	56.90
9			0.890	9.83			2.86	24.80	5.88	59.80	5.99	65.35
10	.179	2.13	0.861	10.76	1.404	15.13	2.40	27.68	4.48	70.15	4.406	71.65
12	.161	2.45	0.807	12.51	1.250	17.98	1.85	32.05	2.52	77.95	2.355	79.60
14	.148	2.75	0.749	14.19	1.146	20.58	1.585	35.66	1.34	82.10	0.833	83.20
16	.139	3.04	0.728	15.72	1.026	22.95	1.415	38.84	0.588	84.10	0.350	84.50
18	.132	3.29	0.662	17.14	0.940	25.10	1.306	41.70	0.298	85.00	0.235	85.20
20	.125	3.53	0.615	18.46	0.869	27.05	1.241	44.40	0.211	85.60	0.172	85.70
25	.111	4.11	0.518	21.39	0.738	31.37	1.104	50.57	0.127	86.45	0.093	
30	.104	4.63	0.426	23.89	0.629	35.06	0.980	56.35	0.085	87.00	0.058	86.85
35	.092	5.13	0.379	26.00	0.554	38.28	0.836	61.20	0.061	87.45	0.037	
40	.085	5.58	0.341	27.90	0.505	41.08	0.718	65.30	0.045	87.75	0.027	87.40
45	.079	5.96	0.315	29.60			0.625	68.85	0.032	87.95	0.020	
50	.074	6.34	0.291	31.17	0.438	46.16	0.539	71.90	0.020	88.05		87.60
60	.066	7.01	0.251	34.02	0.391	50.65	0.407	77.10		88.15	0.000	87.80
70	.060	7.61	0.220	36.60	0.350	54.65	0.278	80.65				
80	.055	8.16	0.197	38.82	0.314	58.25	0.197	83.15				
90	.051	8.67	0.177	40.80	0.277	61.45	0.139	84.95				
100	.048	9.14	0.157	42.55	0.247	64.25	0.086	86.20				
120	.044	10.01			0.199	69.10						
140	.040	10.81			0.165	73.00						
160	.036	11.53			0.139	76.30						
180	.044	12.21			0.119	79.15						
200	.041	13.00			0.101	81.50						
220	.037	13.74			0.079	83.45						
240	.033	14.41			0.058	84.85						
260	.030	15.03										

- (b) liberation of nascent carbon, which, according to the author's opinion, acts as an efficient catalyser for this reaction;
- (c) action of the boundary between the new phase of minute crystal of CaCN_2 formed and the reacting CaC_2 .

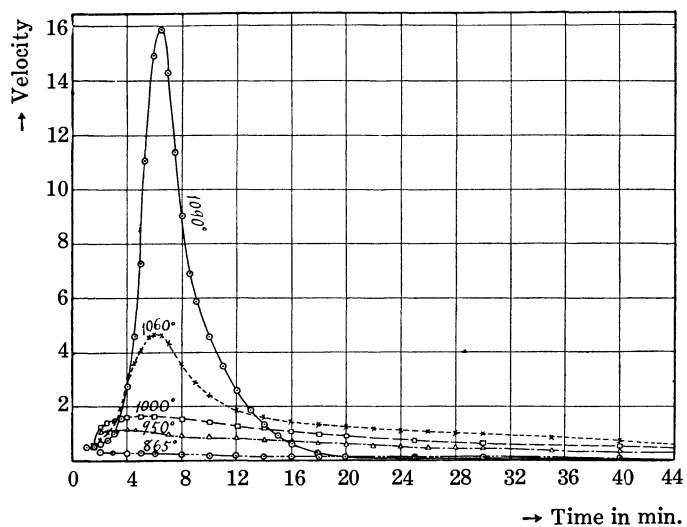


Fig. 1.—Reaction velocity and temperature.

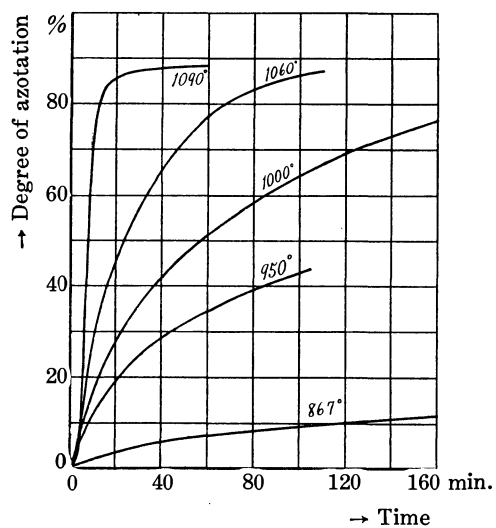


Fig. 2.—Degrees of azotation and temperature.

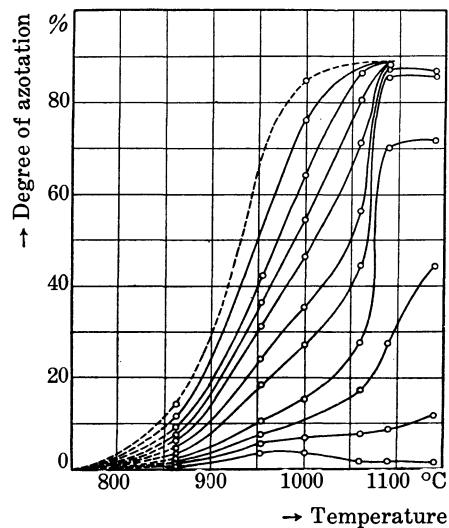


Fig. 3.—Degrees of azotation after definite times at various temperatures.

The time of the maximum velocity increases with rising temperature, and the degree of azotation (Y) at that time also increases with temperature as shown by the following equation.

$$\log Y = A - \frac{B}{T},$$

where A and B are constants and T the absolute temperature. (See Table 2 and Fig. 4).

Table 2.

Exp. No.	361	359	362	360	363	365
$1/T \times 10^4$	8.78	8.18	7.86	7.50	7.34	7.08
Y	0.65	2.44	6.80	12.56	21.43	36.0
$\log Y$	-0.19	0.39	0.83	1.10	1.31	1.55

The simple relation for the first order of the reaction velocity does not hold generally in this case, and the following integrated form does not give a constant value of k_4 .

$$k_4 = \frac{1}{t-t_0} \ln \left(\frac{n_\infty - n_0}{n_\infty - n_t} \right) \dots \dots \dots (4_1)$$

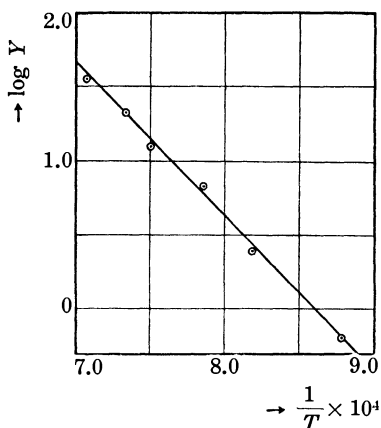


Fig. 4.—Relations btw. degrees of azotation (Y) before the time of velocity maximum and temperature.

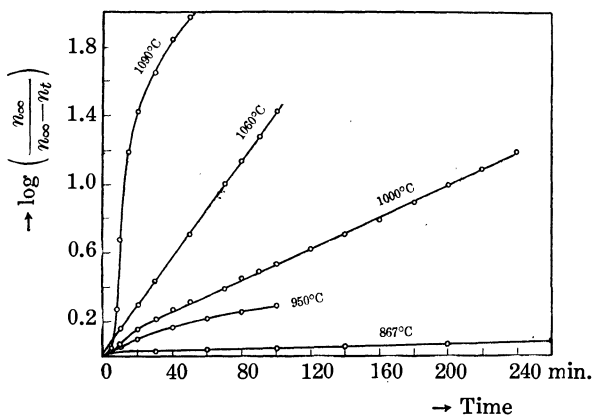


Fig. 5.—Relation btw. $\log \left(\frac{n_\infty}{n_\infty - n_t} \right)$ and time at various temps. (Powdered carbide).

where n_0 and n_t (%) are degrees of azotation at time t_0 and t (minutes) respectively, n_∞ the final maximum value of n_t , and k_4 a velocity constant.

As is shown in Fig. 5 and Table 3, the results at 1000° and 1060°C. satisfy the following relation after a certain time from the beginning,

$$k'_4 = \frac{2.303}{t+t'} \log \left(\frac{n_\infty}{n_\infty - n_t} \right) \dots\dots\dots (4_2)$$

in which k'_4 and t' being constant. We have then

$$n_t = n_\infty (1 - e^{-k'_4(t+t')}) \dots\dots\dots (4_3)$$

Table 3. Powdered carbide.

Relation btw. $\log_{10} \left(\frac{n_\infty}{n_\infty - n_t} \right)$ and time at various temperatures.

Exp. No.	361	359	362	360	363
Temp. °C	867	950	1000	1060	1090
t , min.					
5					0.0457
10		0.0558	0.068	0.160	0.6741
20		0.1007	0.153	0.297	1.4178
30	0.0233		0.212	0.430	1.6484
40		0.1661	0.261		1.8525
50			0.308	0.704	1.9717
60	0.0354	0.2095			
70			0.388	1.000	
80		0.2489	0.446	1.132	
90			0.490	1.284	
100	0.0469	0.2824	0.534	1.421	
120			0.620		
140	0.0561		0.708		
160			0.797		
180			0.891		
200	0.0686		0.989		
220			1.085		
220			1.183		
260	0.0806				

Applying this relation to the data obtained from Exp. 360 at 1060°C., for example, we have $k_4' = 0.0320$, $t' = 1.5$ and therefore

$$n_t = 89.6 \{1 - e^{-0.0320(t+1.5)}\} \dots\dots\dots (4_4)$$

The values calculated by the equation (4₄) fairly well agree with the observed ones as shown in Table 4.

Table 4.

t	k_4'	n_t (obs.)	n_t (calc.)
10	0.0321	27.68	27.6
20	0.0318	44.40	44.5
30	0.0315	56.35	57.8
50	0.0315	71.90	72.5
70	0.0322	80.65	80.5
80	0.0323	83.15	83.0
90	0.0323	84.95	84.8
100	0.0322	86.20	86.2
110	0.0318	87.00	87.1
Mean 0.0320			

At temperatures lower and higher than 1000–1060°C., the above relation is not fulfilled. At 950° and 867°C. the following relation, which was derived from the assumption that the layer of products retards the reaction,⁽¹⁾ was found to be satisfied:

$$\frac{\{n_{\infty}^{\frac{1}{3}} - (n_{\infty} - n_t)^{\frac{1}{3}}\}^2}{t - t'} = k_5' \dots\dots\dots (4_5)$$

where t' and k_5' being constant (Table 5). If we draw curves of $\{n_{\infty}^{\frac{1}{3}} - (n_{\infty} - n_t)^{\frac{1}{3}}\}^2$ against time, we have straight lines in the cases of Exp. 359 (950°C.) and 361 (867°C.). (Fig. 6).

Of course the relation 4₅ is not fulfilled at temperatures above 1000°C., and even at 867°C. it does not hold, if the carbide is mixed with catalysers such as active carbon (Exp. 521 at 867°C.) and calcium chloride (Exp. 523 at 867°C.), which are effective to accelerate the reaction. (See Table 5, Exp. No. 521; the numerical value of n_t will be found in the next paper).

(1) Vid. the next paper.

Table 5. Powdered carbide.

Relation between $\left\{n_{\infty}^{\frac{1}{3}} - (n_{\infty} - n_t)^{\frac{1}{3}}\right\}^2$ and time at 867° and 950°C.

Exp. No.	361		359		362	363	(521)
Temp. °C.	867		950		1000	1090	(867)
Time. min.	{ } ²	<i>k</i> ₅ '×10 ⁴	{ } ²	<i>k</i> ₅ '×10 ⁴	{ } ²	{ } ²	{ } ²
10	0.00639	2.74	0.0576	92.9	0.25	3.35	0.0036
20			0.152	93.8		9.50	.0100
30			0.250	95.4		11.6	.0196
40			0.336	92.8		13.8	.0306
50			0.429	92.9		16.0	.0420
60	0.0146	2.74	0.518	92.2	1.145	.0566 (at <i>t</i> =62)	
70			0.609	92.0			
80			0.706	92.7			
90	0.0253	2.72	0.784	91.0	1.99		
100			0.865	90.0			
120							
140	0.0361	2.71			2.92		
180					4.97		
200	0.0530	2.74			7.21		
240	0.0703	2.77					
260							
<i>t</i> '	6.7		3.8				
Mean <i>k</i> ₅		2.737		92.57			

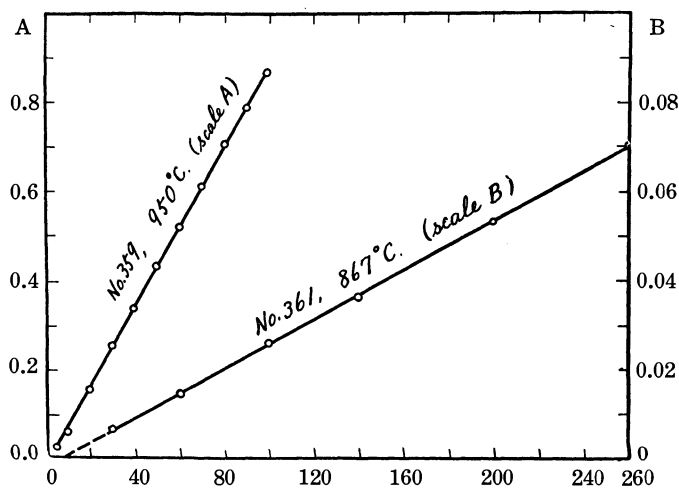


Fig. 6.— $\left\{n_{\infty}^{\frac{1}{3}} - (n_{\infty} - n_t)^{\frac{1}{3}}\right\}^2$ against time.

From the equation 4₅ we have

$$n_t = n_\infty - \left\{ n_\infty^{\frac{1}{3}} - \sqrt[3]{k'_5(t-t')} \right\}^3 \dots\dots\dots (4_6)$$

The calculated values of n_t by this equation coincide fairly well with the observed ones. (Table 6).

Table 6. Exp. No. 361.

$$(n_\infty = 99.0; t' = 6.7 \text{ min}; k'_5 = 2.737 \times 10^{-4})$$

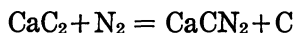
t , min.	30	60	100	140	200	260
n_t (obs.)	4.63	7.01	9.14	10.81	13.00	15.03
n_t (calc.)	4.68	7.00	9.21	10.93	13.05	14.82

The theoretical consideration of these relations will be given in the next paper.

Applying the Arrhenius' equation

$$\ln k = C - \frac{E}{RT} \dots\dots\dots (4_7)$$

on the results obtained from Exps. No. 362 and 360, we have the apparent heat of activation E for the reaction



at the temperature between 1000 and 1060°C.:

$$E = 4.57 \log \left(\frac{k'_{T_1}}{k'_{T_2}} \right) / \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \dots\dots\dots (4_8)$$

If we assume $N_\infty = 90.0$ in both cases, then we have $k_4 = 0.0309$ for 1060°C. and 0.0107 for 1000°C., and putting these values in the equation (4₈) we have $E = 58.6$ Cal./mol. for the temperatures between 1000 and 1060°C. Above the temperature of about 1080°C. the velocity increases suddenly and E becomes smaller (about 33 Cal./mol.). This may be due to the change in the phase of the reacting substance, e.g. partial fusion of the system $\text{CaC}_2 - (\text{CaCN}_2) - \text{CaO} - \text{CaF}_2$.⁽¹⁾ At the same time the character of the velocity curve deviates from Equation 4₂, and

(1) H. H. Franck and H. Heimann, *Z. Elektrochem.*, **33** (1927), 469, reported that the lowest melting point of the system $(\text{CaC}_2 - \text{CaF}_2 - \text{CaO})$ is 1070°C.

also the reaction is too fast to be measured accurately at such higher temperatures.

These experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co., Ltd., Tokyo, before Sept. 10th, 1930, and reported to the meeting of directors and engineers of the company on that day. The author expresses his best thanks to Mr. K. Hibi, who gave him the opportunity of carrying out the experiments and allowed him to publish this report now, and to Mr. I. Kobayashi, who assisted him during the experiment.

Summary.

The effect of temperature elevation to the velocity of azotation of powdered calcium carbide (with 1% CaF_2) has experimentally been determined.

1. At a constant temperature lower than about 950°C ., the following relation was found:

$$n_t = n_\infty - \left\{ n_\infty^{\frac{1}{3}} - \sqrt{k'_5(t-t')} \right\}^3$$

where n_t means the degree of azotation (in %) after a time t , and n_∞ the final and maximum value of n_t ; k'_5 and t' are constants.

2. At a constant temperature between about 1000 and 1060°C ., the common monomolecular course was found, namely:

$$n_t = n_\infty \left\{ 1 - e^{-k'_4(t+t')} \right\}$$

where k'_4 being a velocity constant.

3. At any temperature there is a maximum in the velocity; the time and the degree of azotation at the maximum point increase with rising temperatures. The following approximate relation was found between them.

$$\log Y = A - \frac{B}{T},$$

where Y is the degree of azotation at the maximum of the velocity, T the absolute temperature, and A and B constants.

4. From the temperature coefficient of the velocity constant, the apparent heat of activation for a powdered technical carbide (with 1% CaF_2) was calculated to be about 58.6 Cal./mol. at temperatures between 1000° and 1060°C ., and about 33 Cal./mol. above 1080°C .

Research Laboratory of the Denki-Kagaku-Kogyo Co., Ltd.,
Yurakucho, Kojimachi-ku, Tokyo.

INFLUENCE OF TEMPERATURE ON THE COAGULATION OF SILVER HALIDE SOLS AND OF ARSENIC TRISULFIDE SOL.

By Tominosuke KATSURAI.

Received June 18th, 1932. Published August 28th, 1932.

In a previous paper a short note was given of the coagulation of silver halide sols and of arsenic trisulfide sol which were prepared according to the description of Wo. Ostwald.⁽¹⁾ In this experiment a porcelain beaker was used to contain the sol in heating it in the autoclave. Hydrogen sulfide was not removed from the arsenic sulfide sol used for the experiment.⁽²⁾

The present experiment was undertaken with the view to pursue the study in greater detail and to get more exact information as to the nature of coagulation. In heating the sol in an autoclave it is probable that the porcelain itself is affected by the sol above 100°C. and thus the dissolved impurities from the porcelain may cause some change to the coagulation. In order to get rid of this defect a transparent flask of fused quartz with the capacity of 100 c.c. was used in the present experiment. The results of experiments are given in each case.

Experimental.

Silver halide sols. The sols were prepared by mixing of dilute solution of potassium halide with silver nitrate solution, in the following three different proportions, viz.

(1) *In equivalent proportions.* 1 c.c. of 0.1N. potassium halide was diluted to 100 c.c. with water. This diluted solution was poured into 1 c.c. of 0.1N. silver nitrate which had been contained in a beaker.

(2) *Excess of silver nitrate.* 1 c.c. of the potassium halide solution and 2 c.c. of the silver nitrate solution were used.

(3) *Excess of potassium halide.* 2 c.c. of the potassium halide solution and 1 c.c. of the silver nitrate solution were used. The procedures of preparation both in (2) and (3) were same as in (1).

First the coagulation at 100°C. was studied. Test tubes of hard glass were used in this case. The test tubes, each containing the sols,

(1) T. Katsurai, *Sci. Pap. Inst. Phys. Chem. Research.* **12** (1929), 166.

(2) Cf. Wo. Ostwald: *Practical Colloid Chemistry*, (1926), 6-8.

were heated by the boiling water in a beaker, which was heated from below, and the coagulation taking place thereby was observed.

The three sols, viz. the AgCl-, AgBr- and AgJ-sol of (1) were noticeably turbid as soon as they were prepared indicating that they are unstable. At 100°C. these sols as well as the AgCl-sols of (2) and (3) completely coagulated and settled on the bottom of the test tubes. The sols of other composition viz. the AgBr- and AgJ-sol of (2) and (3) seemed to be very stable against the action of heat, and therefore their coagulation was studied by heating them in an autoclave. The procedure of the autoclave treatment was the same as was described in a previous paper,⁽¹⁾ the only difference being that the flask of quartz was used.

At 120°C. the AgBr- and AgJ-sol of (2) coagulated completely. It was at 180°C. that the AgBr-sol of (3) coagulated completely and settled. The temperature below 180°C. was not sufficient to cause complete coagulation. The AgJ-sol of (3) was the most stable and coagulated almost completely when it was heated at 200°C.

Arsenic trisulfide sol. The sol was prepared by blowing hydrogen sulfide into a solution of arsenious oxide.⁽²⁾ After the sol formation was complete the excess of hydrogen sulfide was removed by blowing a bubble of air into the sol for half an hour.

The coagulation was studied at 160°, 180° and 200°C. At 160°C. the colour of the sol changed to deep yellow and there was formed some precipitate on the bottom. At 180°C. this tendency predominated. At 200°C. almost of the sol was coagulated and settled on the bottom and the upper part of the sol was almost clear. This is quite different from the sol from which hydrogen sulfide was not removed and which dissolved completely at 180°C. It is suggested that the amount of hydrogen sulfide contained in the sol plays a important rôle in the process of coagulation.

With the intention of testing if there is any difference of light absorption between the two sols (the one from which hydrogen sulfide was not removed, and the other from which hydrogen sulfide was removed by a stream of air) the measurement was carried out within the range of visible light.⁽³⁾ But there was no noticeable difference between them.

(1) T. Katsurai, *Sci. Pap. Inst. Phys. Chem. Research*, **13** (1930), 89.

(2) Cf. Wo. Ostwald: *loc. cit.*

(3) The measurement was carried out by Mr. S. Fukushima.

Summary.

(1) The coagulation of silver halide sols which takes place when they were subjected to heating in an autoclave was studied. It was observed that the sols prepared by using an excess of potassium halide, especially the AgJ-sol in an excess of potassium iodide, were most stable against the action of heat.

(2) The arsenic trisulfide sol from which hydrogen sulfide was removed shows noticeable coagulation at 180° and 200°C. This behaviour is quite different from that of the sol from which hydrogen sulfide was not removed.

(3) The light absorptions of arsenic trisulfide sols, one which is free from hydrogen sulfide and the other containing hydrogen sulfide, were compared. No noticeable difference was observed.

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

THE SURFACE TENSIONS OF ETHYL ETHER, ACETONE, TOLUENE AND METHYL ALCOHOL AT LOW TEMPERATURE.

By Tokuzo TONOMURA and Kaoru CHUJO.

Received June 1st, 1932. Published August 28th, 1932.

The surface tensions of ethyl ether, acetone, toluene and methyl alcohol were measured by means of the capillary rise method. Out of many tubes three capillary tubes, which were considered to have uniform cross sections, were selected, and two marks, say a and b, were etched on them as reference points. The diameters of the capillary tubes were measured with the mercury columns of known weight at point to point, and they were taken against the distances from the reference points a or b as the calibration curves. Each of the capillary tubes, then, was sealed in a tube of about 16 cm. in length and 3 cm. in diameter, as shown in Fig. 1. The tube c was connected to the vacuum loading apparatus which was the same as that in the previous paper.⁽¹⁾

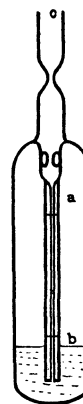


Fig. 1.

(1) Tonomura and Uehara, this bulletin, 6 (1931), 118.

The materials used for the present experiments were obtained from Kahlbaum pure chemicals and were purified by the ordinary ways. Their boiling points were as follows:

Ethyl ether, 34.28–34.30°C./757.2 mm.; Acetone, 55.98°C./753.4 mm.;
Toluene, 109.71–109.80°C./764.9 mm.; Methyl alcohol, 64.89–64.95°C./764.9 mm.

The apparatus sealed off from the loading apparatus was set in the large brass block which was hanged from the ceiling to prevent any disturbances due to the motion of cryostat and others, and to keep vertically. The cryostat and thermometer were the same as those used in the previous experiments.⁽¹⁾

Table 1.
Surface tensions of ethyl ether.

Temp. °C.	Height. cm.	Radius. cm.	$D^{(2)}-d^{(3)}$	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
30.00	1.561	0.02856	0.6982	15.25	15.52	A
„	2.277	0.01973	„	15.37	„	B
25.00	1.609	0.02856	0.7046	15.87	16.11	A
„	2.359	0.01973	„	16.07	„	B
— 1.00	2.694	0.01973	0.7367	19.12	19.24	B
— 18.85	2.926	„	0.7585	21.46	21.49	B
— 22.48	2.993	„	0.7616	22.04	21.94	B
— 40.68	2.218	0.02857	0.7821	24.28	24.28	A
— 45.05	3.273	0.01973	0.7869	24.91	24.84	B
— 51.14	3.299	0.02857	0.7936	25.54	25.64	A
— 59.68	2.369	„	0.8033	26.64	26.78	A
— 63.02	3.501	0.01973	0.8070	27.32	27.23	B
— 70.30	2.454	0.02856	0.8149	27.99	28.21	A
— 72.85	3.612	0.01973	0.8173	28.54	28.54	B
— 80.43	2.552	0.02856	0.8249	29.47	29.56	A
— 85.20	3.744	0.01973	0.8299	30.04	30.14	B
— 93.41	3.852	„	0.8385	31.23	31.34	B
— 94.75	2.686	0.02856	0.8400	31.58	31.53	A
—108.24	4.026	0.01973	0.8542	33.25	33.42	B

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 2.2261 \quad (\tau \rightarrow 8.62)$$

(1) Tonomura and Uehara, this bulletin, **6** (1931), 118.

(2) Keyes and Felsing, *J. Am. Chem. Soc.*, **41** (1919), 589.

(3) Curt Ferdinand Mundel, *Z. physik. Chem.*, **85** (1913), 450.

The height of the meniscus in the capillary tube above the liquid surface together with the mark a or b, were observed by a cathetometer through the transparent part of the cryostat. From the distance between the meniscus and the mark, the diameter of the capillary tube at the position of meniscus was determined with the calibration curve which had been obtained previously. The variation of the diameter due to thermal contraction was neglected, as the expansion coefficient of glass was too small to make appreciable errors in the present experiments.⁽¹⁾

The experimental results were shown in Table 1, 2, 3 and 4, and diagrammatically shown in Fig. 2 and 3. The surface tensions γ of the

Table 2.
Surface tensions of Acetone.

Temp. °C.	Height. cm.	Radius. cm.	$D(\omega) - d(\omega)$	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
30.00	1.954	0.02856	0.7797	21.32	21.72	A
„	2.856	0.01973	„	21.53	„	B
20.00	2.045	0.02856	0.7911	22.64	22.98	A
„	2.979	0.01973	„	22.79	„	B
- 1.44	3.288	„	0.8153	25.92	25.75	B
-14.86	3.431	„	0.8302	27.54	27.52	B
-18.14	3.495	„	0.8338	28.17	27.96	B
-25.25	3.551	„	0.8416	28.89	28.92	B
-35.16	3.690	„	0.8523	30.41	30.26	B
-36.87	2.567	0.02586	0.8542	30.68	30.50	A
-44.15	3.792	0.01973	0.8620	31.60	31.50	B
-44.88	2.625	0.02586	0.8628	31.69	31.60	A
-57.32	2.716	„	0.8761	33.30	33.33	A
-66.88	2.798	„	0.8863	34.71	34.68	A
-75.72	4.150	0.01973	0.8957	35.93	36.07	B
-81.65	2.916	0.02856	0.9019	36.81	36.79	A
-86.41	4.255	0.01973	0.9069	37.30	37.47	B
-91.09	2.989	0.02856	0.9118	38.14	38.15	A

$$\gamma \left(\frac{M}{D} \right)^2 = 1.8516 (\tau + 1.808)$$

-
- (1) The apparatus was constructed by ordinary soda glass, whose expansion coefficient is the order of 10^{-5} .
 (2) Felsing and Durban, *J. Am. Chem. Soc.*, **48** (1926), 2885.

liquid in the fifth columns of the tables were calculated with the following formula:

$$\gamma = -\frac{1}{2}g r \left(h + \frac{r}{3} \right) (D-d)$$

where r is the diameter of the capillary tube, and g the acceleration due to gravity, that is 980.1 cm./sec.² at Sendai. D and d are the

Table 3.

Surface tensions of toluene.

Temp. °C.	Height. cm.	Radius. cm.	$D^{(1)} - d$.	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
20.00	3.362	0.01973	0.8659	28.14	28.12	B
"	2.681	0.02466	"	28.05	"	C
10.50	3.473	0.01973	0.8755	29.40	29.36	B
"	2.774	0.02466	"	29.35	"	C
— 0.00	2.876	0.02466	0.8842	30.72	30.70	C
— 6.33	3.669	0.01973	0.8904	31.59	31.53	B
— 10.00	2.967	0.02466	0.8940	32.06	32.02	C
— 15.46	3.771	0.01973	0.8994	32.79	32.75	B
— 20.13	3.056	0.02466	0.9039	33.39	33.37	C
— 25.73	3.886	0.01973	0.9093	34.16	34.13	B
— 30.05	3.136	0.02466	0.9135	34.63	34.71	C
— 35.52	4.003	0.01973	0.9187	35.55	35.46	B
— 41.07	3.230	0.02466	0.9241	36.08	36.21	C
— 44.74	4.103	0.01973	0.9273	36.78	36.71	B
— 50.67	3.315	0.02466	0.9332	37.39	37.54	C
— 55.10	4.214	0.01973	0.9373	38.18	38.15	B
— 60.25	3.398	0.02466	0.9421	38.69	38.86	C
— 66.20	4.325	0.01973	0.9476	39.62	39.69	B
— 70.30	3.484	0.02466	0.9514	40.06	40.27	C
— 76.10	4.451	0.01973	0.9568	41.16	41.09	B
— 81.30	3.596	0.02466	0.9615	41.79	41.82	C
— 85.85	4.558	0.01973	0.9657	42.54	42.47	B
— 92.25	3.704	0.02466	0.9714	43.49	43.38	C
— 96.50	4.677	0.01972	0.9753	44.08	43.99	B

$$\gamma \left(\frac{M}{D} \right)^{\frac{2}{3}} = 2.4109 \quad (\tau = 39.05)$$

(1) Tonomura and Uehara, this bulletin, **6** (1931), 255.

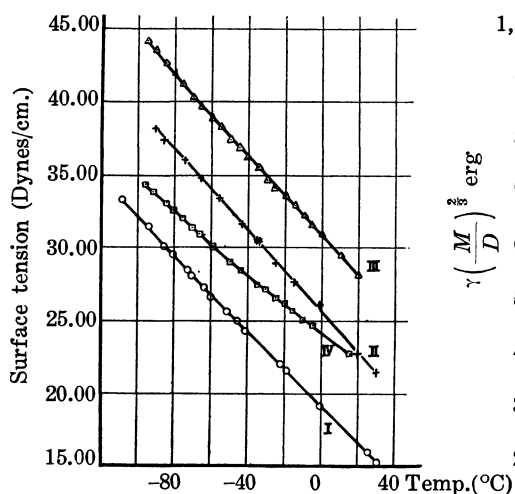
densities of liquid and vapour respectively. The values of D and d used were found in the literatures given in the foot note of the tables. When the values of d were not found in the literatures, they were calculated from the vapour pressure, assuming that the vapour obeys the ideal gas law. The letters in the last columns of the tables represent the capillary tubes used in the measurements.

Table 4.
Surface tensions of methyl alcohol.

Temp. °C	Height. cm.	Radius. cm.	$D-d^{(1)}$	γ (obs.) Dynes/cm.	γ (calc.) Dynes/cm.	Capil.
25.00	2.861	0.01973	0.7882	21.80	21.75	B
”	2.288	0.02466	”	21.80	”	C
15.00	2.945	0.01973	0.7970	22.69	22.70	B
”	2.354	0.02466	”	22.67	”	C
— 0.36	2.456	0.02466	0.8106	24.06	24.04	C
— 5.63	3.131	0.01973	0.8154	24.69	24.57	B
—10.91	2.528	0.02466	0.8205	25.07	25.10	C
—16.54	3.226	0.01973	0.8255	25.75	25.67	B
—20.60	2.600	0.02466	0.8293	26.05	26.09	C
—25.11	3.298	0.01973	0.8334	26.58	26.58	B
—31.78	2.685	0.02466	0.8397	27.24	27.25	C
—34.67	3.383	0.01973	0.8424	27.56	27.56	B
—40.24	2.743	0.02466	0.8476	28.10	28.15	C
—44.00	3.466	0.01973	0.8512	28.53	28.56	B
—49.83	2.811	0.02466	0.8569	29.11	29.19	C
—55.13	3.565	0.01973	0.8619	29.71	29.77	B
—59.42	2.875	0.02466	0.8662	30.10	30.25	C
—66.12	3.671	0.01973	0.8729	30.98	31.00	B
—70.26	2.958	0.02466	0.8770	31.36	31.47	C
—74.66	3.758	0.01973	0.8813	32.02	31.97	B
—80.72	3.038	0.02466	0.8873	32.54	32.67	C
—84.43	3.854	0.01973	0.8911	33.20	33.10	B
—91.27	3.124	0.02466	0.8981	33.91	33.91	C
—94.75	3.970	0.01973	0.9017	34.61	34.32	B

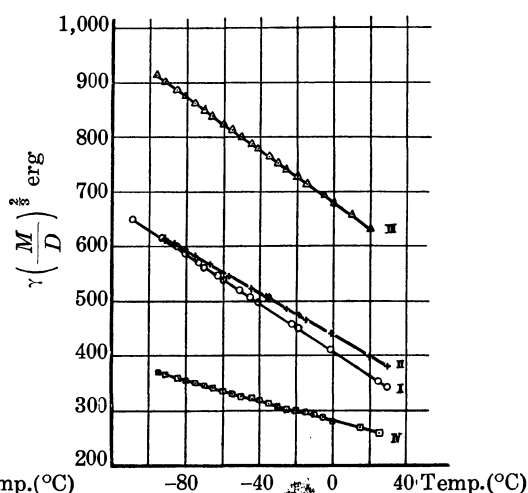
$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 560.89 - 1.12481T + 0.000333186T^2$$

(1) Körber, Ann. Physik., (4), **37** (1912), 1012.



I. Ethyl ether II. Acetone
III. Toluene IV. Methyl alcohol

Fig. 2.



I. Ethyl ether II. Acetone
III. Toluene IV. Methyl alcohol

Fig. 3.

The values of γ in the sixth columns of the tables were calculated from the empirical formula of the Eötvös type given at the end of the tables. They were obtained from the experimental values of γ with the method of the least square. M in those formulae is the molecular weight of the substances and τ is the temperature measured from the critical temperature, which is 194.5°C . for ethyl ether, 235.6°C . for acetone and 320.8°C . for toluene. In the case of methyl alcohol whose molecules were considered to be much associated, the constants suitable for the Eötvös formula were not found and a quadratic formula, therefore, was used, where T is the absolute temperature.

In conclusion, the present authors thank to Prof. S. Mitsukuri for his helpful guidance during their experiments.

The Laboratory of Theoretical Chemistry, Faculty of Science,
Tohoku Imperial University, Sendai.

May, 1932.

VAPOUR PRESSURE OF RHENIUM HEPTOXIDE, VAPOUR PRESSURE AND DISSOCIATION PRESSURE OF RHENIUM OCTOXIDE.

By Eijiro OGAWA.

Received June 7th, 1932. Published August 28th, 1932.

As a rule the elements of the 7th group stand in closer relationship to the elements of the 8th group than to those of the 6th group. Rhenium also resembles osmium in many points. For example its oxides, rhenium heptoxide and rhenium octoxide, are volatile without decomposition as is the case in osmium tetroxide, while the oxides of tungsten are not so. In 1929 I. and W. Noddack published their laborious work on these two rhenium oxides. The present author reinvestigated the properties of these substances and found that some of them do not agree with their description. It has been found that rhenium heptoxide does not decompose at its boiling points, $363^{\circ}\text{C}.$, and so its vapour pressure can be measured. It is true that rhenium octoxide already slightly dissociates into rhenium heptoxide and oxygen at ordinary temperature, but the partial pressure of oxygen is very small even at $220^{\circ}\text{C}.$, and the vapour pressure of rhenium octoxide can therefore be measured, although accurate values can not be expected.

Experimental Part.

Considering the fact that the result of I. and W. Noddack was obtained by using only one gr. of the metal soon after its discovery, it may be somewhat uncertain. The author found that the results of the preliminary experiments did not well agree with their results as following.

1. The oxides prepared by Noddacks may be not perfectly anhydrous. As rhenium octoxide and heptoxide are both very hygroscopic according to the author's experiments, it would be insufficient to dry the oxygen by merely passing one sulphuric acid bottle, one calcium chloride tube and one phosphorus pentoxide tube as they used in their experiments. Noddacks found that the heptoxide melts at $220^{\circ}\text{C}.$, a temperature which is very much lower than the author's value, $298^{\circ}\text{C}.$ This fact indicates that the lower value obtained by them is probably due to the presence of water resulting from insufficient drying of the gas.

(1) I. and W. Noddack. Z. Anorg. Chem. 181, 1-37, (1929).

2. They stated that heptoxide easily changes to octoxide by heating in oxygen. The author found that this is not the case, the reaction $2\text{Re}_2\text{O}_8 \rightarrow 2\text{Re}_2\text{O}_7 + \text{O}_2$ being almost irreversible.

3. According to Noddacks heptoxide changes to blue lower oxide by heating above 300°C . in a vacuum. It does not, however, decompose at least at its boiling point, 363°C ., in the author's experiment.

4. They described in page 11 that crude rhenium heptoxide prepared must be heated in N_2 at 170°C . for 10 minutes in order to convert mixed octoxide to heptoxide. For completing the reaction, however, it has been found desirable to keep in a reduced pressure at 180 – 190°C . for one or two hours.

5. They stated in page 13 that rhenium heptoxide have a large vapour tension even at 150°C ., but the author found its tension at 150°C ., was only 3.0 mm.

Vapour Pressure of Rhenium Heptoxide. *Dry of Oxygen.* Oxygen from a bomb was passed into one sulphuric acid washer, two calcium chloride tubes, 3 cm. in diameter and 80 cm. in length, and one empty 2 liter flask and then four phosphorus pentoxide tubes of the same size as the calcium chloride tubes. A spring manometer, one phosphorus pentoxide tube, and four sulphuric acid washers were next connected. All of these connections were made in glass. Velocity of oxygen was 30 c.c. or 40 c.c. per minute.

Apparatus and Preparation. The apparatus was shown in Fig. 1. After cleaning with hot HNO_3 solution of $\text{K}_2\text{Cr}_2\text{O}_7$, the entire system was evacuated to 0.0001 mm. for several hours. The sensibility of this spring manometer was 0.01 mm. 2 Gr. of rhenium was taken into a porcelain boat. At the beginning of heating, a small quantity of Re_2O_8

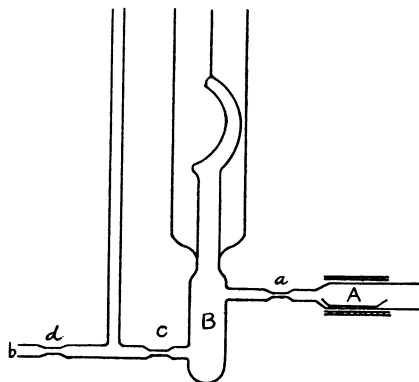


Fig. 1.

was formed, which adhered to the wall of the apparatus, but soon changed to yellow Re_2O_7 on heating with flame. When all of rhenium had sublimated, the apparatus was sealed at a and d. In order to convert octoxide, which might still have remained, into rhenium heptoxide, it was heated at 210°C . for 10 minutes and then at 190°C . for 2 hours, the manometer being immersed in a bath of liquid paraffine and evacuated to 0.0001 mm. It was then sealed at c. The detail of the method of the measurement using a spring manometer was already described in the previously published paper on osmium tetroxide.⁽²⁾ The electric furnace used for heating was 15 cm. in internal diameter and 50 cm. in depth. It was 13 cm. long from the bottom of B to the top of the spring. The mercury reservoir of the thermometer was placed at the middle of this interval. The temperature fluctuation of the electric furnace was about $\pm 2.0^\circ\text{C}$. in this interval. Three thermometers were used. Two of these had the range of $100\text{--}200^\circ\text{C}$. and of $200\text{--}300^\circ\text{C}$. respectively, and were graduated into hundredths of a degree. The other had the range of $300\text{--}360^\circ\text{C}$. and was graduated into tenths of a degree. Temperature was so regulated as to be within $\pm 0.3^\circ\text{C}$. by adjusting the current by hand for about four hours. After each measurement temperature was lowered to the ordinary temperature, and no increase in pressure was observed. This shows that any dissociation did not occur. For reading pressure a cathetometer was used and necessary corrections were added to the data. The data up to $1/10$ mm. or

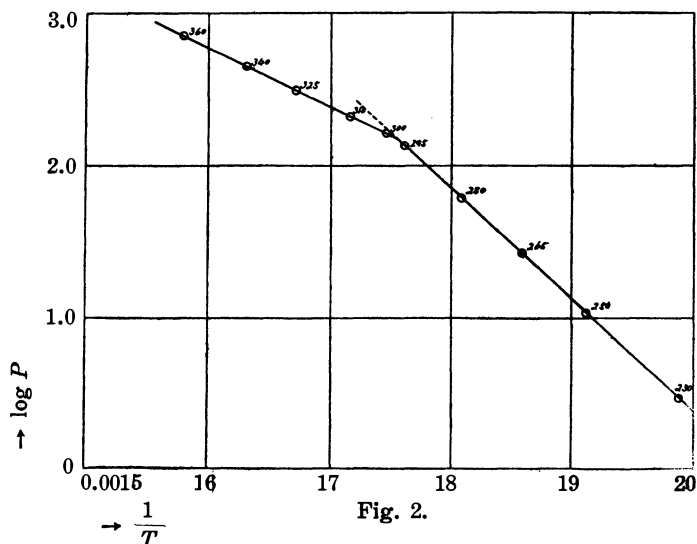


Fig. 2.

(2) This Bulletin, 6 (1931), 302-317.

1 mm. were adopted. Above 340°C. the needle moved a little left or right owing to irregularity of temperature. The vapour pressure soon reached its equilibrium. The relations of $\log P$ and $1/T$ is linear as shown in Fig. 2 and expressed by following August's formulas.

Sublimation:

$$\log P = -7217.95/T + 14.83866.$$

Vaporization:

$$\log P = -3920.13/T + 9.04668.$$

Table 1.

$t^{\circ}\text{C}$	$T^{\circ}\text{abs.}$	$1/T$	P mm.	$\log P$
230	503	0.0019881	3.0	0.47712
250	523	0.0019120	10.9	1.03473
265	538	0.0018587	26.5	1.42325
280	553	0.0018083	61.2	1.78675
295	568	0.0017606	135	2.13033
300	573	0.0017452	160	2.20412
310	583	0.0017153	210	2.32222
325	598	0.0016722	312	2.49415
340	613	0.0016313	449	2.65225
360	633	0.0015798	711	2.85187

Melting Point and Boiling Point. The melting point and the boiling point obtained from Fig. 2 are 297°C. and 363°C. respectively. The observed melting point was 297°C.

Heat of Sublimation. The mean heat of sublimation between 230°C. and 295°C. obtained by the above formula is 33050 cal. The mean heats of sublimation in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH (cal.)
230—250	240	33710
250—265	257.5	33140
265—280	272.5	33020
280—295	287.5	32980

Extrapolating to 297°C. we obtain 32910 cal., which is the heat of sublimation at the melting point.

Heat of vaporization. The mean heat of vaporization between 300°C. and 360°C. obtained from the above formula is 17950 cal. The mean heats of vaporization in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH (cal.)
300—310	305	18080
310—325	317.5	18260
325—340	332.5	17700
340—360	350	17750

The heats of vaporization at the melting point and at the boiling point obtained by extrapolation are 18300 cal. and 17400 cal. respectively.

Heat of fusion. $32910 - 18300 = 14610$ cal.
 Trouton's constant

$$\Delta H/T = 17400/636 = 27.4$$

According to vapour density measurement of Noddack, rhenium heptoxide has a composition of Re_2O_7 at 502°C.

Vapour Pressure and Dissociation Pressure of Rhenium Octoxide.
Apparatus and Preparation. Oxygen was dried in the same way as in the case of heptoxide. Velocity of the gas was 100 c.c. or 110 c.c. per minute. The apparatus used was shown in Fig. 3. A, a spiral tube which was made by coiling twelve times a tube of 6 mm. in diameter, was 5.5 cm. in inner diameter and 9 cm. in height. After the apparatus was cleaned carefully, it was dried thoroughly by heating in a vacuum of 0.0001 mm. 2 Gr. of rhenium was taken. At the beginning of the reaction, rhenium octoxide was so rapidly formed that it escaped through four sulphuric acid washers, but with the scintering of the surface of rhenium its production became less and less until rhenium heptoxide began to deposit near the boat. After all of rhenium sublimated, heptoxide was driven into the spiral. Rhenium octoxide, which is white when pure, owing to the presence of rhenium heptoxide, adhered to the inside of the spiral in somewhat yellow fine powder. The apparatus was then sealed at a and b and kept in a vacuum of 0.0001 mm. at ordinary temperature for ten minutes after which it was sealed at c.

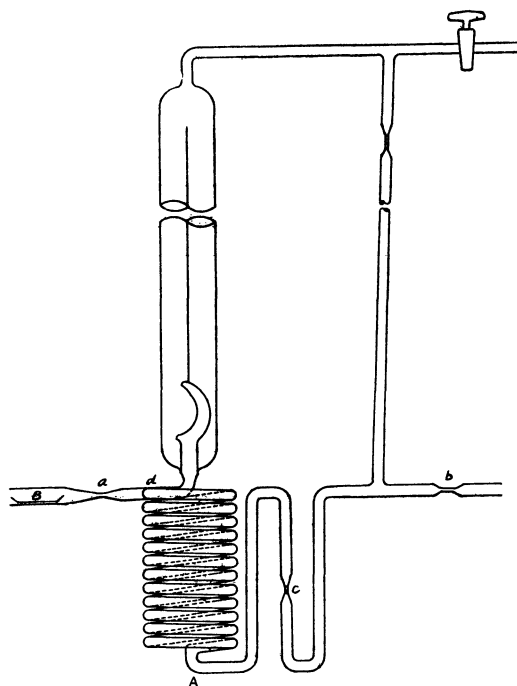


Fig. 3

Dissociation Pressure of Octoxide. For heating, the electric furnace previously described was used. The distance from the bottom of A to the top of the spring was 21 cm. The fluctuation of temperature was $\pm 3^\circ\text{C}$. On heating at 100°C . pressure rose to 10.8 mm. after about 2 hours from the start and it remained constant for four hours. After cooling it became 3.24 mm. at 14.5°C ., which did not change until the next day. The time required to reach the equilibrium pressure became more rapid with rise of temperature. Temperature was maintained constant for four hours in each experiment. Pressure was measured up to 220°C . The results are shown in Table 2. As these increases in pressure did not change during several days, it can be assumed that the reaction $2\text{Re}_2\text{O}_8 \rightarrow 2\text{Re}_2\text{O}_7 + \text{O}_2$ is perfectly irreversible at ordinary temperature. It was assumed that this increase in pressure indicates the dissociation pressures at each temperature, and the equilibrium pressures were calculated by adding necessary corrections. The values obtained in this manner are shown in the 3rd column in Table 2. The linear relations of $\log P$ and $1/T$ are shown in Fig. 4.

Table 2.

$t^{\circ}\text{C}$	$1/T$	O_2 press. (mm.)	$\log P$
100	0.0026810	4.19	0.62221
120	25445	4.73	0.67486
140	24213	5.39	0.73159
160	23095	6.01	0.77887
180	22075	6.63	0.82151
200	21142	7.30	0.86332
220	20284	7.84	0.89432

$$\log P = -416.08/T + 1.73877$$

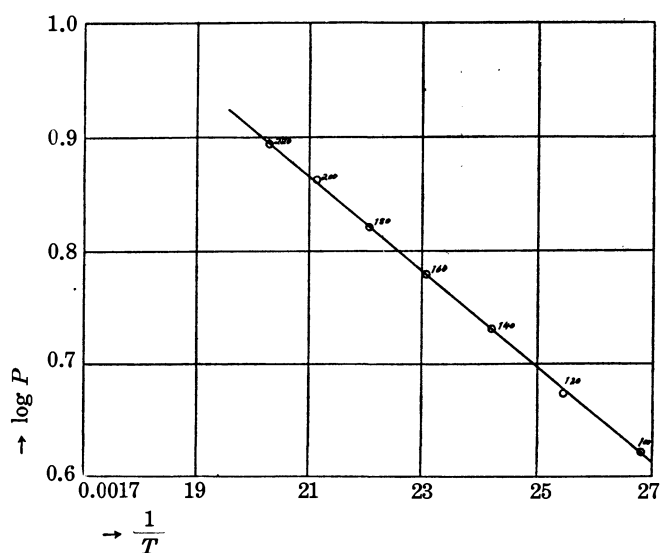


Fig. 4.

Vapour Pressure of Octoxide. The values obtained by subtracting the dissociation pressure from the observed pressures were adopted as the vapour pressure of rhenium octoxide as shown in Table 3. In the apparatus used for the determination of dissociation pressure (Fig. 3) the greater part of the heptoxide was in d, and the octoxide, yellowish white in colour due to the presence of a small quantity of heptoxide, was spread all over the spiral. There was nothing in the spring. After heating to 100°C. a small quantity of white sublimate of rhenium octoxide

was observed in the spring. The quantity of this sublimate increased gradually until the temperature at 220°C. and the inside of the spring was covered with it. This pure white sublimate always existed at each temperature of measurement. It shows that there was an excess of octoxide in the spring at each time of the experiment. The reason why rhenium octoxide on cooling should have assembled in the spring may be due to its being surrounded by the outer tube of reduced pressure or inhomogeneity of temperature of the electric furnace. It was unnecessary to consider the influence of rhenium heptoxide, as octoxide was in pure state. The linear relations between the logarithm

Table 3.

$t^{\circ}\text{C}$	$1/T$	P mm.	$\log P$
100	0.0026810	6.6	0.81954
120	25445	11.7	1.06819
140	24213	18.7	1.27184
160	23095	25.6	1.40824
180	22075	31.8	1.50243
200	21142	39.2	1.59329
220	20284	46.6	1.66839

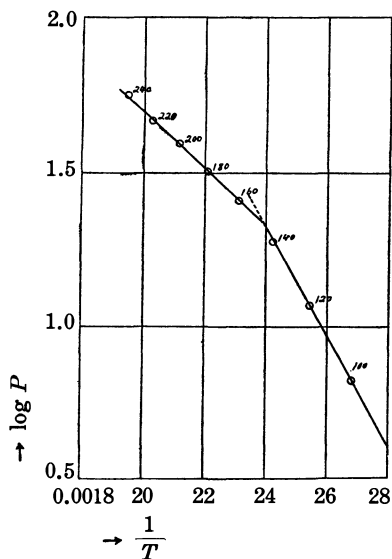


Fig. 5.

of the vapour pressure determined as mentioned above and $1/T$ are shown in Fig. 5. There is a knick at 145°C . It must be the melting point. But this relation can no longer exist above 240°C ., owing to the sublimation of heptoxide. As this sublimated heptoxide dissolves in the melted octoxide in the spring it is not possible to calculate the vapour pressure of Re_2O_8 .

Sublimation:

$$\log P = -1738.74/T + 5.48512$$

Vaporization:

$$\log P = -924.18/T + 3.54384$$

Heat of Sublimation. The mean heat of sublimation between 100°C . and 140°C . is 7960 cal. Those in more limited ranges are as follows.

Temperature range	Mean temperature	ΔH
100—120	110	8340
100—140	120	7970
120—140	130	7570

Extrapolating to 145°C . 7000 cal. is obtained.

Heat of Vaporization. The mean heat of vaporization between 160° and 220°C . is 4230 cal. Those in more limited temperature ranges are as follows.

Temperature range	Mean temperature	ΔH
160—200	180	4340
180—200	200	4240
160—220	180	4230

The mean heat of vaporization at the melting point obtained by extrapolation is 4500 cal.

Heat of fusion. $7000 - 4500 = 2500$ cal.

Chemical Institute, Faculty of Engineering,
Kyushu Imperial University, Fukuoka.

June, 1932.

STUDIES ON REACTIONS BETWEEN GAS AND SOLID. V. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF SIZE OF GRAIN ON ITS VELOCITY.

By Takeo AONO.

Received May 27th, 1932. Published August 28th, 1932.

Experimental.

Experiment A. A block of a technical carbide was crushed by a mill and sieved in three parts: H = (less than 80 mesh), I = (48–80 mesh) and J = (larger than 80 mesh), and H and I were put in reaction with nitrogen in the same reaction tube at 1030°C. for 3 hrs. "Granular carbide"⁽¹⁾ (larger than 48 mesh) added with 5% of calcium fluoride was also subjected to azotation at 1030°C. for 4 hours. Table 5₁ shows the results.

If we assume that the particles are spheres of initial mean radius r_0 , which was changed chemically to the depth r' , then the ratio of the remaining carbide to the initial is given by Equation (5₁):

Table 5₁.

No. and date of the exp.	Crushed carbide		Granular carbide	
	No. 302 (June 18, 1930)		No. 304 (June 20, 1930)	
	H	I	I	H
Sieves (mesh)	<80	80–48	5–8	8–48
Mean radius (r_0) mm.	0.044	0.117	1.59	0.664
Yield of acetylene (G) c.c./gr. at 15°C.	219.5	264.9	228.0	229.4
Temp. (°C.) and time (hrs.)	1030°; 3	1030°; 3	1030°; 4	1030°; 4
Gr. of samples taken (W)	2.3908	3.3696	2.6606	2.9925
Increase in weight $\div W = (w)$	0.0644	0.0321	0.0602	0.1150
Degrees of azotation %	36.0	12.7	23.6	48.7
Yield of acetylene G c.c./gr.	67.6	189.1	139.5	67.3
$(1+w)G'/G = \alpha$	0.325	0.750	0.650	0.337
α , corrected for efflorescence*	0.413	—	—	—
$1 - \frac{2}{3}\sqrt{\alpha}$	0.255	0.091	0.134	0.304
Thickness of reacted layer (r') mm.	0.011	0.011	0.213	0.201

* This correction is due to the change $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$, $\text{Ca(OH)}_2 + \text{CaC}_2 = 2\text{CaO} + \text{C}_2\text{H}_2$ (by heating) and $\text{C}_2\text{H}_2 = 2\text{C} + \text{H}_2$, which has been determined by the author. The numerical value is given by

$$\frac{67.6 \times 1.0644}{219.5 - (264.9 - 219.5)} = 0.413.$$

(1) Vid. the former paper.

$$\alpha = \frac{(r_0 - r')^3}{r_0^3} = \frac{G'(1+w)}{G}, \dots\dots\dots (5_1)$$

$$r' = (1 - \sqrt[3]{\alpha}) r_0 \dots\dots\dots (5_2)$$

From these experiments r' , namely $\int_0^t \left(\frac{dr'}{dt}\right) dt$, is found to be independent of the initial size r_0 of the particles (at 1030°C.). Whether the value $\left(\frac{dr'}{dt}\right)$ is dependent on time or not is the next problem to be determined, mined.

Experiment B. The method was the same as that of reported in the former papers,⁽¹⁾ the velocity of azotation being determined from time to time by measuring the absorption speed of nitrogen at constant temperature (1140°C.) and pressure (1 atm.). The samples were the "granular" of diameters (0.175–1.0), (1.0–2.0), (2.0–3.0) mm. respectively. The sample of Exp. 376 was (3.17–0.84 mm.) different from others, all being free from catalysers. Table 5₂ and Fig. 1 show the results.

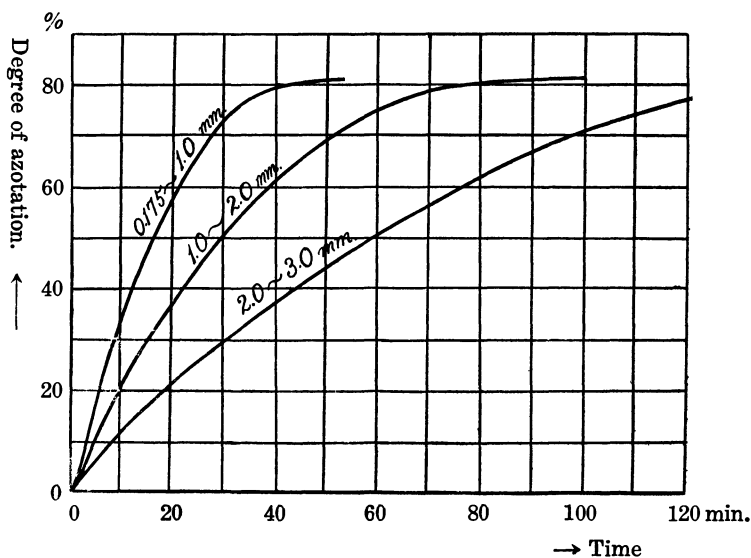


Fig. 1.—Azotation of "granular carbide" of varying size at 1140°C.

(1) This bulletin, 7 (1932), 143.

Table 5₂.

Velocity of azotation of "Granular carbide" of various size at constant temp. (1140°C.) and pressure (1 atm.) of nitrogen (without catalysers).

Exp. No.	389		390		386		376	
Dia. mm.	0.175—1.0		1.0—2.0		2.0—3.0		3.17—0.84	
Purity %	63.9		71.3		72.6		62.9	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	(1.0)	1.18	1.07	1.05	0.578	0.73	1.11	1.70
2	(2.00)	4.86	1.25	3.48	0.695	2.08	1.30	4.08
3	2.00	9.61	1.25	6.10	0.688	3.53	1.35	6.61
4	1.80	14.23	1.19	8.65	0.660	4.94	1.36	9.19
5	1.60	18.26	1.07	10.98	0.623	6.28	1.35	11.75
6	1.47	21.88	1.04	13.17	0.595	7.55	1.33	14.28
7	1.36	25.27	1.00		0.578		1.32	16.78
8	1.30	28.46	1.00	17.36	0.540	9.93	1.29	19.25
9	1.24		0.909		0.525		1.27	21.68
10	1.20	34.38	0.909	21.29	0.525	12.18	1.24	24.05
12	1.11		0.862		0.510		1.18	28.63
14	1.03	45.00	0.833		0.490		1.12	33.02
15	0.99		0.815	30.17	0.475	17.40		
16	0.95		0.769		0.461		1.06	37.40
18	0.885		0.685		0.438		0.995	41.10
20	0.81	58.10	0.699	37.92	0.422	21.99	0.939	44.75
25	0.64	66.60	0.614	44.73	0.390	26.22		
30	0.45	73.30	0.570	50.90	0.370	30.18	0.703	60.02
35	0.265	77.55			0.360	33.98		
40	0.110	79.65	0.440	61.50	0.350	37.66	0.464	71.1
45	0.060		0.377		0.339			
50	0.020	81.00	0.350	69.65	0.325	44.78	0.192	77.0
60	0.000	81.15	0.220	75.30	0.300	51.30	0.064	79.2
70			0.110	78.90	0.270	57.30	0.028	79.9
80			0.047	80.40	0.240	62.65	0.000	80.0
90			0.023	81.10	0.210	67.35		
100			0.000	81.35	0.180	71.35		
120					0.105	77.35		
140					0.042	80.15		
160					0.014	81.10		

If we calculate the values

$$\left\{ n_{\infty}^{\frac{1}{3}} - (n_{\infty} - n_t)^{\frac{1}{3}} \right\} / t = k_5 \dots\dots\dots (5_3)$$

where n_t denotes the degree of azotation in % at time t , and n_{∞} the final value of n_t , k_5 is found to be nearly constant. (Table 5₃).

Table 5₃.

Velocity constant k_5 for granular carbide at 1140°C.

Exp. No.	389		390		386		376		385	
Dia. mm.	0.18—1		2—1		3—2		3.17—0.84		2—1	
+ $C_a F_2$, %	0		0		0		0		4	
Time, min.	n_t	k_5	n_t	k_5	n_t	k_5	n_t	k_5	n_t	k_5
5	18.26	0.0704	10.98	0.0408	6.28	0.0230	11.75	0.044	10.92	0.040
10	34.38	0.0725	21.29	0.0417	12.18	0.0228	24.05	0.048	23.25	0.046
20	58.10	0.0742	37.92	0.0408	21.99	0.0216	44.75	0.051	39.70	0.043
30	73.30	0.0780	50.90	0.0403					53.07	0.043
40	79.65	0.0796	61.50	0.0406	37.66	0.0202	71.1	0.056	64.10	0.043
50	81.00	0.0760	69.65	0.0412					72.35	0.044
60			75.30	0.0418	51.30	0.0204	79.2	0.055	77.70	0.045
70			78.90	0.0426					80.40	0.045
80			80.40	0.0418	62.65	0.0210	80.0	0.056		
90			81.10	0.0410					81.70	0.044
100			81.35	0.0412	71.35	0.0217				
120					77.35	0.0228				
140					80.15	0.0230				
160					81.10	0.0227				
∞	81.15		81.36		81.45		80.0		81.90	
mean k_5		(0.0751)		0.0413		0.0219		0.052		0.0435

Theoretical considerations.

For the velocity of azotation of a spherical carbide grain of an initial mean radius r_0 at a given temperature and pressure, we suppose the following relations:

Case a.

The linear velocity of azotation in the direction of r is constant :

$$-\frac{dr}{dt} = \kappa \dots\dots\dots (5_a)$$

where r : radius at any time t ,
 κ : velocity constant.

$$\therefore \kappa = \frac{r_1 - r}{t - t_1} \dots\dots\dots (6_a)$$

If $r_1 = r_0$ at $t_1 = 0$, then

$$\kappa_0 = \frac{r_0 - r}{t} \dots\dots\dots (7_a)$$

$$\therefore k_5 = \frac{\{n_\infty^{\frac{1}{3}} - (n_\infty - n_t)^{\frac{1}{3}}\}}{t} \dots\dots (8_a)$$

Case b.

the linear velocity is inversely proportional to the thickness of the layer of the product :

$$-\frac{dr}{dt} = \frac{\kappa'}{r_0 - r} \dots\dots\dots (5_b)$$

$(r_0 - r) \propto$ resistance to the proceeding of the reaction.

$$\kappa' = \frac{(r_1 - r) \left\{ r_0 - \frac{1}{2}(r_1 + r) \right\}}{t - t_1} \dots\dots (6_b)$$

$$\kappa'_0 = \frac{(r_0 - r)^2}{t} \dots\dots\dots (7_b)$$

$$\therefore k'_5 = \frac{\{n_\infty^{\frac{1}{3}} - (n_\infty - n_t)^{\frac{1}{3}}\}^2}{t} \dots\dots (8_b)$$

because $r = \nu m^{\frac{1}{3}} = \mu(n_\infty - n_t)^{\frac{1}{3}}$ and $r_0 = \nu m_0^{\frac{1}{3}} = \mu n_\infty^{\frac{1}{3}}$; m : mass of a grain; n_∞ , n_t : degree of nitrogen-fixation, and ν , μ : constants.

From the experimental results, shown in Table 5₃, we see that at temperature of 1140°C. k_5 are almost constant at any time after $t = 10$ minutes from the beginning. Hence, in case of the "granular carbide," the linear velocity of azotation of the carbide towards the center is constant at 1140°C. If we denote the mass of a carbide granule with m , the reactive surface with A , and the density with δ , then from Equation (5_a) we have:

$$-\frac{dm}{dt} = -A \cdot \delta \cdot \frac{dr}{dt} = \kappa \cdot A \cdot \delta, \dots\dots\dots (9_a)$$

$$\text{and also } -\frac{dm}{mdt} = -\frac{d \ln m}{dt} = \kappa \cdot F \cdot \delta, \dots\dots\dots (10_a)$$

where $F = A/m =$ specific surface of the remaining carbide. Hence, the rate of change of the carbide to cyanamide at these higher tem-

peratures and under a constant pressure is proportional to the surface area.

It was already pointed out in the former paper⁽¹⁾ that at temperatures lower than 950°C. and in case of powdered carbide without effective catalysers, the following relation holds good:

$$n_t = n_\infty - \left\{ n_\infty^{\frac{1}{3}} - \sqrt[3]{k'_5(t-t')} \right\}^3 \dots\dots\dots (4_8)$$

$$\text{or} \quad \frac{\{ n_\infty^{\frac{1}{3}} - (n_\infty - n_t)^{\frac{1}{3}} \}^2}{t-t'} = k'_5 = \text{constant} \dots\dots\dots (4_7)$$

This equation coincides with (8_b), although it has a term ($t-t'$) instead of t . This t' is a correction due to the initial disturbance of the velocity, which starts with very low values, and attains a maximum after several minutes. This shows that at temperatures lower than about 950°C., the layer of the products hinders the further progress of the reaction proportionally to the thickness of the layer.

At temperatures, where the products melt partly with the carbide, or when some catalysers such as CaCl_2 were added, the relation is of course different from the above. (See the former papers.⁽¹⁾).

Even at moderate temperatures, it is sometimes found that a velocity-curve at constant pressure involves several fragments of different nature: starting from an initial acceleration- or induction-curve, it passes a maximum point and then describes either a constant linear velocity curve or a curve of the first order and turns finally to a parabolic curve.

These experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co. Ltd., Tokyo, before Sept. 10th (1930), and reported to the meeting of the directors and engineers of the Co. on that day.

Summary.

The effect of size of powder and grain of carbide on the velocity of azotation was experimentally discussed, and it was also experimentally determined that the velocity of azotation of carbide at constant temperature and pressure is

1. proportional to the surface area of individual grains, in case of the "granular" carbide, and the radial velocity of azotation is constant at about 1140°C. or

(1) Aono, loc. cit.

2. the radial velocity is inversely proportional to the thickness of changed layer at 950°C. and lower temperatures.
3. In some cases, there are several types of character in the velocity.

Research Laboratory of the Denki-Kagaku-Kogyo Co. Ltd.,
Yurakucho, Kojimachi-ku, Tokyo.

THE INTERFACIAL TENSIONS BETWEEN HEXANE AND AQUEOUS SALT SOLUTIONS.

By Meiji KIDOKORO.

Received June 30th, 1932. Published August 28th, 1932.

The interfacial tension between two liquids is affected, in general, more or less by a third component which is added to this system. In the system of water and hydrocarbon oil each component has actually no mutual solubility and the added inorganic salt is only soluble in the water phase. Therefore the change of the interfacial tension caused by the concentration change of the salt solution should run parallel to that of the surface tension of the salt solution.

But an unexpected result was obtained in the experiment of McLewis on the interfacial tension of hydrocarbon oil against aqueous solution of metallic salt, namely the lowering of the interfacial tension occurred by the addition of CuCl_2 , AgNO_3 , or KCl .⁽¹⁾ Since each of these substances raises the surface tension of water against air, and does not influence that of the organic liquid, so that the interfacial tension might be expected to be raised.

As McLewis used a dynamical method, while the present experiment was undertaken in order to repeat it statically.

Experimental.

Material. "Normal hexane from petroleum" from Kahlbaum has been used after distillation, the boiling point of which being 68.5°C . and the density 0.6691.

(1) McLewis, *Phil. Mag.*, (6) **17** (1909), 466.

Surface Tension of Aqueous Salt Solution. Ordinary capillary rise method was used, and the capillary rise was read by means of a cathetometer. Calculations were made by the following formula.

$$\alpha = \frac{1}{2} r g h (d - d')$$

where α denotes the surface tension, r radius of the capillary, g gravity constant, h capillary rise, d density of the liquid and d' density of the air.

Meniscus correction for the reading of h was neglected considering the accuracy of the present experiment. For the density of air 0.0012 (at 20°C. under 760 mm. Hg) was taken into calculation. The results are shown in Table 1.

Table 1. at 20°C.

Solute	C (gram-mol per litre)	d	$r = 0.0415$ cm. h (cm.)	α (dyne/cm.)
BaCl ₂	0	0.9982	3.535	71.7
„	0.01	1.0000	3.525	71.8
„	0.05	1.0074	3.510	72.0
„	0.1	1.0162	3.495	72.2
„	0.3	1.0532	3.400	72.8
BaBr ₂	0.01	1.0008	3.530	71.8
„	0.05	0.0112	3.510	72.0
„	0.1	1.0241	3.410	72.2
„	0.3	1.0842	3.335	72.8
NaCl	0.01	0.9986	3.535	71.8
„	0.05	1.0003	3.535	71.9
„	0.1	1.0024	2.530	72.0
„	0.3	1.0095	3.520	72.2
„	0.4	1.0146	3.515	72.5
KCl	0.01	0.9985	3.535	71.8
„	0.05	1.0008	3.535	71.9
„	0.1	1.0030	3.530	72.0
„	0.2	1.0075	3.515	72.1
„	0.3	1.0122	3.505	72.2
KBr	0.01	0.9991	3.535	71.8
„	0.05	1.0039	3.530	71.9
„	0.1	1.0067	3.515	72.0
„	0.2	1.0150	3.495	72.1
„	0.3	1.0233	3.460	72.2

Table 1.—(Concluded)

Solute	C (gram-mol per litre)	d	$r = 0.0415$ cm. h (cm.)	α (dyne/cm.)
KI	0.01	0.9985	3.535	71.8
„	0.05	1.0043	3.525	71.9
„	0.1	1.0104	3.505	72.0
„	0.3	1.0345	3.440	72.2
CuCl ₂	0.01	0.9994	3.530	71.8
„	0.05	1.0043	3.515	72.0
„	0.1	1.0100	3.515	72.2
„	0.2	1.0222	3.480	72.4
„	0.3	1.0343	3.469	72.8
AgNO ₃	0.01	0.9995	3.535	71.8
„	0.05	1.0053	3.525	72.0
„	0.1	1.0120	3.505	72.2
„	0.3	1.0401	3.420	72.4
Ba(NO ₃) ₂	0.01	1.0004	3.530	71.8
„	0.05	1.0090	3.510	72.0
„	0.1	1.0195	3.485	72.2
„	0.2	1.0395	3.425	72.4
[Co(NH ₃) ₆]Cl ₃	0.01	0.9995	3.530	71.8
„	0.05	1.0046	3.520	72.0
„	0.1	1.0106	3.510	72.1
„	0.2	1.0232	3.485	72.2

Some of the above data are plotted on curves in Fig. 1.

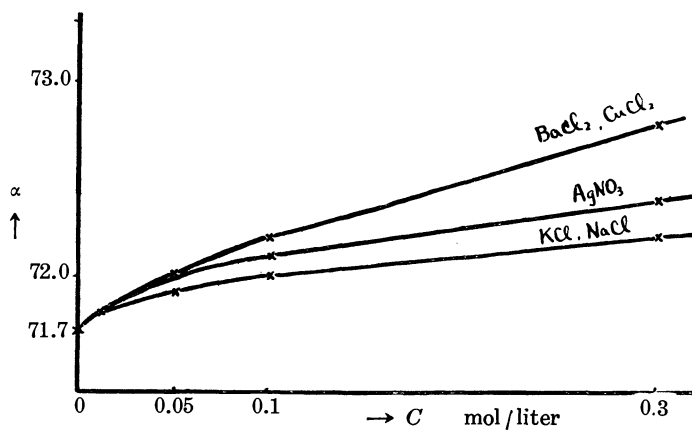


Fig. 1.

The Interfacial Tension. Determinations of the interfacial tensions were made by F. E. Bartell and F. L. Miller's method.⁽¹⁾ The apparatus used is shown in Fig. 2. One of the advantages of this apparatus is that the diameter of the capillary need not be strictly uniform throughout. Calibration of the capillary is necessary only for a given point. It consists of two cups A and B, about 4 cm. in diameter and 10 cm. in height, and these are connected with a U-tube, one arm of which is a capillary of 0.0385 cm. radius.

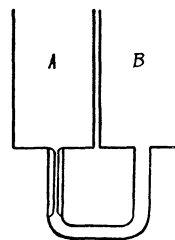


Fig. 2.

The aqueous solution is put into the cup B filling the U-tube. Then oil hexane is introduced into the cup A so that an interface is formed at the top of the capillary. More oil is added drop by drop until the interfacial meniscus is forced back just to the calibrated point. The heights of the liquid in A and B respectively, above the meniscus of the oil, say h and h' , are read by means of a cathetometer. The following condition must be fulfilled in equilibrium.

$$\pi r^2 h d g = \pi r^2 h' d' g + 2 \pi \alpha r$$

where d and d' denote the densities of the liquid in A and B respectively, α the interfacial tension, r the radius of the capillary and g the gravity constant. Therefore

$$\alpha = \frac{1}{2} r g (h d - h' d')$$

The results of the experiment are given in Table 2 and also shown by curves in Fig. 3.

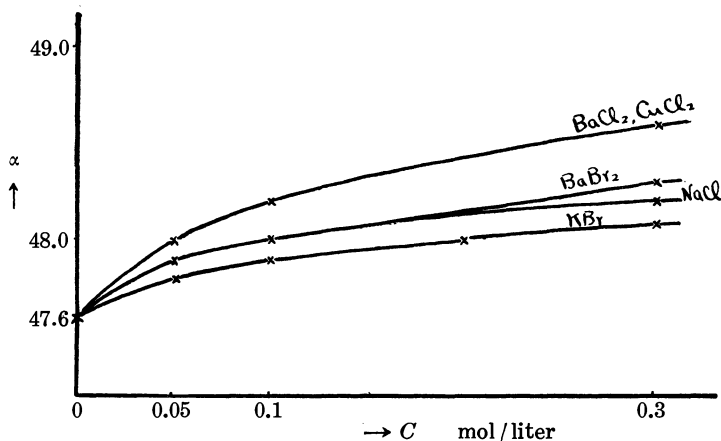


Fig. 3.

(1) F. E. Bartell and F. L. Miller, *J. Am. Chem. Soc.*, **50** (1928), 1961.

Table 2.

Solute	C (gram-mol per litre)	h (cm.)	h' (cm.)	$h d - h' d'$	α (dyne/cm.)
BaCl ₂	0	10.290	4.355	2.539	47.6
"	0.05	9.350	3.670	2.559	48.0
"	0.1	9.070	3.445	2.567	48.2
"	0.3	8.885	3.180	2.590	48.6
BaBr ₂	0.01	8.807	3.345	2.545	47.8
"	0.05	8.510	3.115	2.549	47.9
"	0.1	8.290	2.290	2.557	48.0
"	0.3	8.810	3.090	2.572	48.3
NaCl	0.05	7.905	2.735	2.552	47.9
"	0.1	8.615	3.195	2.558	48.0
"	0.3	9.370	3.670	2.566	48.2
"	0.4	8.615	3.145	2.573	48.3
KCl	0.05	8.855	3.370	2.554	47.9
"	0.1	10.080	4.170	2.559	48.0
"	0.2	9.632	3.855	2.561	48.1
"	0.3	9.775	3.915	2.566	48.2
KBr	0.05	8.885	3.410	2.545	47.8
"	0.1	9.175	3.665	2.551	47.9
"	0.2	7.665	2.525	2.559	48.0
"	0.3	8.990	3.375	2.561	48.1
KI	0.05	8.795	3.330	2.541	47.7
"	0.1	9.375	3.690	2.543	47.8
"	0.3	8.925	3.300	2.558	48.0
CuCl ₂	0.05	8.560	3.155	2.559	48.0
"	0.1	9.645	3.850	2.568	48.2
"	0.2	8.930	3.335	2.570	48.3
"	0.3	8.685	3.115	2.589	48.6
Ba(NO ₃) ₂	0.05	8.425	3.055	2.555	48.0
"	0.1	9.270	3.570	2.564	48.2
"	0.2	9.720	3.785	2.572	48.3
AgNO ₃	0.05	8.525	3.140	2.548	47.9
"	0.1	9.515	3.655	2.554	48.0
"	0.3	9.185	3.445	2.566	48.2
Co(NH ₃) ₆ Cl ₃	0.05	9.490	3.790	2.543	47.8
"	0.1	8.630	3.185	2.556	48.0
"	0.2	9.010	3.385	2.566	48.2

As we see from the table, the results indicate that, on the contrary to that of McLewis, the interfacial tension of aqueous salt solutions against hexane increase by the increase in concentration of the former, and that the interfacial tension runs approximately parallel to that of the surface tension of the salt solution against air.

Dynamical Measurement of the Interfacial Tension. Drop number method was also tried for the measurement of the interfacial tension to compare the results with that of the statical method. Results obtained by two types of dropping pipette coincided to each other and nearly coincided to that obtained by statical method as shown in Table 3. Calculations were made by the following formula.

$$\alpha = \alpha_0 \frac{n_w(d-d_0)}{n(d_w-d_0)}$$

where α_0 : interfacial tension between water and hexane; n_w : drop number of water in hexane; n : drop number of solution in hexane; d_w : density of water; d : density of solution; d_0 : density of hexane.

Table 3.

Solute	C (gram-mol per litre)	n	α (dynamical)	α (statical)
BaCl ₂	0	294	47.6	47.6
„	0.05	301	47.8	48.0
„	0.1	309	48.0	48.2
„	0.3	338	48.4	48.6
BaBr ₂	0.05	303	47.7	47.9
„	0.1	317	47.9	48.0
„	0.3	359	48.2	48.3
CuCl ₂	0.05	297	47.7	48.0
„	0.1	302	47.9	48.2
„	0.3	325	48.2	48.6
NaCl	0.1	297	47.8	48.0
„	0.4	305	48.1	48.3
KBr	0.2	306	47.8	48.0
„	0.3	316	48.0	48.1

The writer wishes to thank Professor J. Sameshima, under whose kind suggestion this work was carried out.

Summary.

The interfacial tensions between aqueous inorganic salt solutions and hexane have been measured by both statical and dynamical method. Results indicate that the interfacial tensions increase by the increase in concentration of the salt solutions, being nearly parallel to the surface tension of the salt solutions.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

STUDIES ON REACTION BETWEEN GAS AND SOLID. VI. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF CATALYSERS ON ITS VELOCITY.⁽¹⁾

By Takeo AONO.

Received May 27th, 1932. Published September 28th, 1932.

It has been known that the most effective and technically important catalysers for the reaction of calcium carbide with nitrogen to form calcium cyanamide are chloride and fluoride of calcium.⁽²⁾ In the present work the effects of catalysers of various kinds in various quantities upon some kinds of technical carbide have been experimentally studied.

Experimental.

1. **Calcium Fluoride.** The samples of carbide (powdered) and the method employed were similar to those of the former experiments for the determination of the effect of temperature upon the same reaction. The results are shown in Table 1 and Figs. 1 and 2. The temperature was kept at 1000°C. The samples of carbide of Exp. No. 362, 375, 391, 392, 393, 394 were the same, while that of No. 425 was taken from another source. Fig. 2 was obtained from Fig. 1 by integrating the velocity graphically and comparing the final values with the results of analyses of the products.

Similar results were obtained with "granular carbide," which was prepared by K. Hibi's method in a spherical grain of about 1-2 mm. in diameter. The temperature was kept at 1140°C. (Tables 2, 3 and Fig. 3). Taking the quantity of calcium fluoride added to the carbide as abscissa, and the time (in min.) required to reach definite degrees of azotation as ordinate, we have Fig. 4.

From these experimental results we see that there is an optimum quantity of fluoride to be added to the carbide, as was reported by F. Foerster and H. Jacoby.⁽³⁾ The optimum quantity is a function of reaction temperature and kinds of carbides; for instance, no effect being perceived by adding CaF_2 at 870°C.

It is also interesting that the point of the maximum velocity is also a function of the quantities of CaF_2 added, the larger the quantity, the later comes the point (Table 4).

(1) Read before the meeting of the Chemical Society of Japan in Dec. 1931.

(2) F. Foerster and H. Jacoby, *Z. Elektrochem.* **12** (1907), 101. G. Bredig, W. Fraenkel and E. Wilke, *ibid.* **13** (1907), 605. Polzenius, D. R. P. Nr. 163320, Kl. 12k (1901).

(3) F. Foerster and H. Jacoby, *Z. Elektrochem.* **12** (1907), 101.

Table 1.

Azotation velocity of powdered carbide with various quantities
of calcium fluoride at const. temp. of 1000°C.

Exp. No.	375	391	392	393	394	425
+CaF ₂	6 <i>u</i> *	11 <i>u</i>	4 <i>u</i>	2.5 <i>u</i>	1 <i>u</i>	0 <i>u</i>
CaC ₂ %	66.8	64.2	68.5	69.5	70.6	74.4
Sample, gr.	3.0012	3.3011	3.0929	3.0011	3.0012	3.0135
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %
1		0.07	0.14	0.09	0.09	0.175
2		0.07	0.08	0.30	0.13	0.24
3	0.068	0.09	0.46	0.20	0.72	0.30
4	0.10	0.11	0.14	0.29	0.24	0.33
5	0.15	0.14	0.18	0.40	1.21	0.41
6	0.18	0.83	0.17	0.53	1.89	0.73
7	0.21	1.23	0.20	2.81	1.21	4.54
8	0.31	1.72	0.23	2.03	7.56	0.325
9	0.38	2.36	0.26	2.64	4.06	0.315
10	0.47	3.11	0.30	3.44	11.50	0.303
12	0.80	5.33	0.43	4.50	15.29	0.294
14	1.25	9.01	0.63	7.87	18.34	0.283
16	2.015	15.22	0.90	14.54	23.36	0.26
18	2.02	22.75	1.19	24.62	27.63	0.24
20	1.84	29.96	1.43	33.83	31.36	0.22
25	1.08		1.14	39.54	34.55	0.203
30	0.82	50.97	0.96	37.21	37.21	0.185
35	0.63		0.73	56.90	43.10	0.160
40	0.53	62.95	0.55	62.90	48.25	0.155
45	0.43		0.45	67.45	15.08	0.146
50	0.32	70.72	0.37	71.10	56.60	0.135
60	0.21	75.60	0.19	79.10	60.40	0.128
70	0.13	78.35	0.10	81.35	63.90	0.12
80	0.09	80.00	0.06	83.60	69.85	0.104
90	0.06	81.30	0.03	84.75	74.45	0.10
100				85.55	78.05	0.095
120	0.05	82.20	0.025	85.55	80.40	0.088
140	0.02	83.15	0.013	86.50	82.15	0.080
160			0.007	86.65	84.25	0.077
180			0.004	86.15	85.45	0.074
200			0.003	86.20	85.85	0.068
					86.20	41.25

* To the author's regret, the unit "*u*" cannot be explained here.

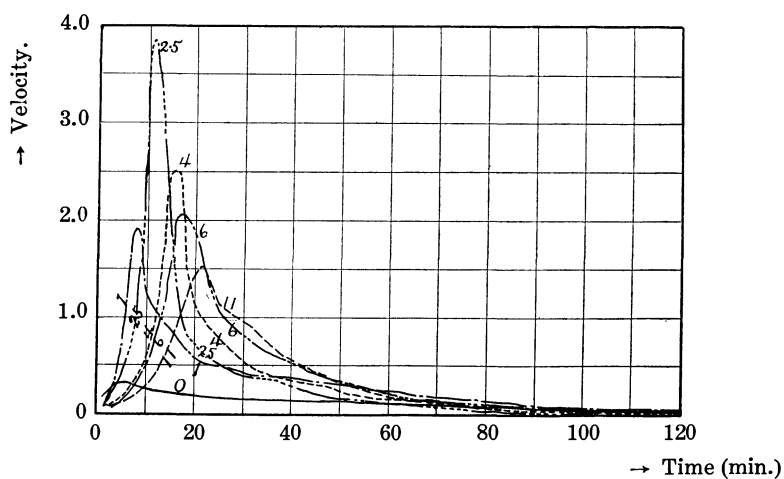


Fig. 1. Azotation velocity of powdered carbide at 1000°C., the numbers on the curves indicating the quantity of CaF_2 added. (in unit "u").

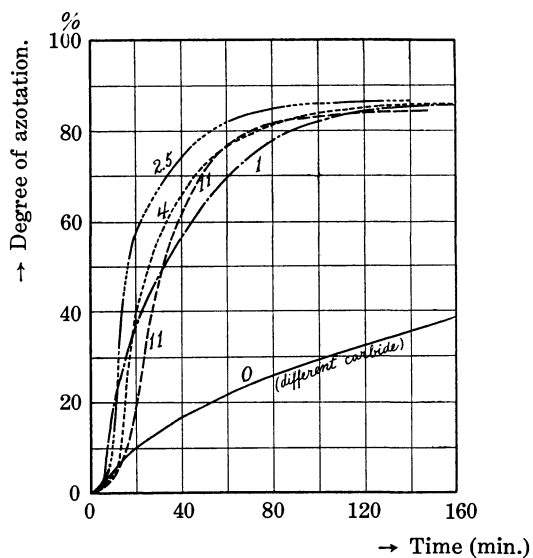


Fig. 2. Effect of CaF_2 upon the azotation of powdered carbide at 1000°C. The numbers on the curves indicate the quantity of CaF_2 added (in unit "u").

Table 2.

Azotation velocity of "granular carbide" with calcium fluoride
at constant temp. of 1140°C. Using reaction tube A.

Exp. No.	376		378	379
+CaF ₂	0		0	3 <i>u</i>
Carbide %	62.9		72.1	69.2
Sample gr.	3.0036		3.0043	3.0004
Time, min.	vel.	fix. %	vel.	fix. %
1	1.11	1.70	0.68?	(0.54)
2	1.30	4.08	0.833	1.99
3	1.35	6.61	0.82	4.33
4	1.36	9.19	0.78	7.75
5	1.35	11.75	0.73	11.72
6	1.33	14.28	0.68	15.32
7	1.32	16.78	0.66	18.32
8	1.29	19.25	0.63	21.00
9	1.27	21.68	0.61	25.70
10	1.24	24.05	0.60	
12	1.18	28.63	0.58	29.73
14	1.12	33.02	0.55	33.34
16	1.06	37.40	0.51	36.58
18	0.995	41.10	0.50	39.68
20	0.939	44.75	0.49	42.58
25			0.44	49.65
30	0.701	60.02	0.415	55.75
35			0.38	61.40
40	0.464	71.10	0.35	66.35
45				0.24
50	0.192	77.0	0.26	75.60
60	0.064	79.2	0.175	80.00
70	0.025	79.9	0.080	81.55
80	0.000	80.0	0.025	81.70
90			0.000	

Table 3.

Azotation velocity of "granular carbide" with calcium fluoride
at constant temp. of 1140°C. Using reaction tube B.

Exp. No.	390		382		383		384		385	
+CaF ₂	0		6 <i>u</i>		10 <i>u</i>		2 <i>u</i>		4 <i>u</i>	
Carbide %	72.3		68.1		65.2		70.3		69.3	
Sample, gr.	3.0008		3.0029		3.0029		3.0030		3.0010	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	1.07	1.05		(0.09)	0.167	0.22	0.213	0.33	0.541	0.68
2	1.25	3.48	0.133	0.38	0.220	0.68	1.00	1.55	0.788	2.13
3	1.25	6.10	0.290	1.04	0.267		1.92	5.20	1.30	4.51
4	1.19	8.65	0.371	2.04	0.308	1.94	1.50	9.11	1.37	7.75
5	1.07	10.98	0.425	3.29	0.353		1.40	12.48	1.37	10.92
6	1.04	13.17	0.500	4.73	0.395	3.60	1.25	15.50	1.25	
7	1.00		0.565	6.36	0.423		1.15	18.10	1.15	16.58
8	1.00	17.36	0.588	8.12	0.447	5.64	0.97	20.35	1.07	
9	0.909		0.605	9.94	0.470		0.88	22.35	0.92	21.25
10	0.909	21.29	0.590	11.75	0.490	7.88	0.84	24.25	0.84	23.25
12	0.862		0.545	14.88	0.510	10.28	0.76	27.82	0.788	26.90
14	0.838		0.513	18.42	0.522	12.77	0.74	31.12	0.730	
16	0.769		0.485	21.45	0.525	15.30	0.70	34.25	0.705	33.62
18	0.685		0.460	24.32	0.520	17.84	0.67	37.20	0.667	
20	0.699	37.92	0.445	27.06	0.510	20.29	0.62	40.00	0.640	39.70
25	0.614	44.73	0.405		0.485		0.55		0.59	
30	0.570	50.90	0.390	39.68	0.460	31.82	0.51	52.30	0.55	53.07
35			0.375		0.440		0.46		0.49	
40	0.440	61.50	0.350	51.10	0.415	42.48	0.415	62.80	0.42	64.10
45	0.377			56.25	0.393		0.365		0.375	
50	0.350	69.65	0.300	61.00	0.370	51.90	0.310	70.90	0.31	72.35
60	0.220	75.30	0.210	69.35	0.320	60.20	0.204	76.60	0.17	77.70
70	0.110	78.90	0.150	74.90	0.270	67.30	0.105	79.90	0.08	80.40
80	0.047	80.40	0.080	78.30	0.200	73.00	0.095	81.45	0.025	
90	0.023	81.10	0.040	80.00	0.135	77.10	0.020	82.10	0.000	81.70
100	0.000	81.35	0.021	80.55	0.075	79.50	0.000	83.13		
120			0.000	80.75	0.010	81.15				

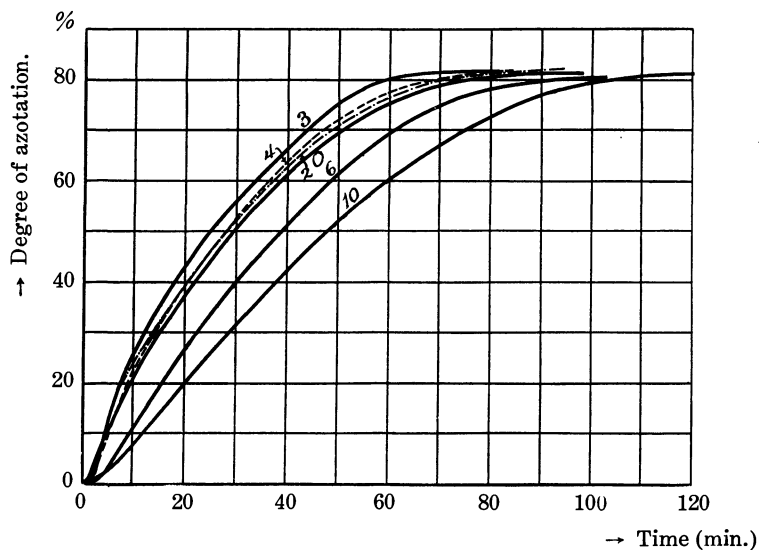


Fig. 3. Effect of CaF_2 upon the azotation of "granular carbide" of 71.0% purity at 1140°C . The numbers on the curves indicate the quantity of CaF_2 added. (in unit "u").

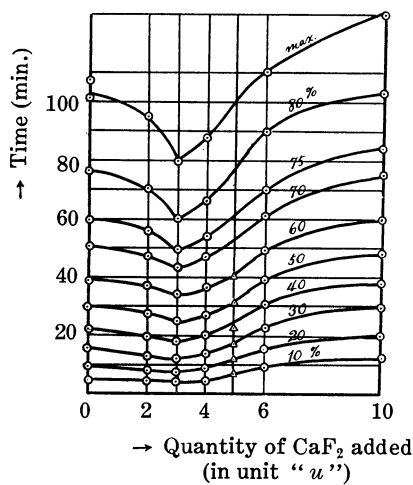


Fig. 4. Time (min.) required to attain to the equal degrees of azotation and the effect of CaF_2 added to the granular carbide of 1 ~ 2 mm. dia. ($\text{CaC}_2 = 71.0\%$)

Table 4.

Effect of CaF_2 upon the time of the velocity maximum.a) Powdered carbide at 1000°C .

Exp. No.	425	394	393	392	375	391
+ CaF_2	0 <i>u</i>	1 <i>u</i>	2.5 <i>u</i>	4 <i>u</i>	6 <i>u</i>	11 <i>u</i>
Time of vel. max. (min.)	4.5	8.0	11.3	15.-16.5	17-18.5	21.5

b) "Granular carbide" at 1140°C .

Exp. No.	378	384	379	385	382	383
+ CaF_2	0 <i>u</i>	2 <i>u</i>	3 <i>u</i>	4 <i>u</i>	6 <i>u</i>	10 <i>u</i>
Time of max. vel. (min.)	2.0-2.5	2.5	4.5-5.0	3.2	9.0	15.0-19.0

2. **The Slag of a Phosphorus Furnace.** This material was prepared from the slag produced by the reaction of phosphate rock and carbon to prepare phosphorus in an electric furnace. The analysis of the slag is as follows (the components are calculated provisionally as oxides):

P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	Total CaO
1.29	18.36	1.75	16.55	49.40%

The effect upon the azotation velocity of calcium carbide is seen in Table 5.

It is very interesting that the slag has not only the accelerating effect, but it also diminishes the time to maximum velocity; the velocity decreases soon after less than two minutes from the beginning, and it is rather uncertain whether the maximum point really exists or not.

Table 5.

Effect of a phosphorus slag added
3% to the powdered carbide ($\text{CaC}_2 = 74.4\%$) at 1000°C .

Exp. No.	421		425	
Slag %	3		0	
Sample, gr.	3.0037		3.0135	
Time	vel.	fix. %	vel.	fix. %
1		(2.57)	0.175	0.29
2	1.21	5.15	0.24	
3	1.08		0.30	0.87
4	0.855	10.45	0.33	1.51
5	(0.730)		0.33	2.19
6	0.625	13.63	0.325	
7	0.590		0.315	3.53
8	0.555	16.18	0.303	
9	0.529		0.294	
10	0.500	18.38	0.283	5.39
20	0.332	26.80	0.185	10.14
30	0.262	33.10	0.155	13.54
40	0.228	38.35	0.135	16.56
60	0.173	46.90	0.104	21.53
80	0.150	53.85	0.095	25.56
100	0.133	59.90	0.080	29.20
120	0.118	65.25	0.077	32.45

3. **Calcium Chloride.** The action of calcium chloride is eminent even at lower temperatures. There is a point of maximum velocity also in this case; the details will be given later with others.

4. **Effect of Carbon and Carbon-containing Substances.** In the previous paper⁽¹⁾ the author expressed his opinion that the nascent carbon liberated by the reaction, $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$, will be acting as an eminent catalyser for this reaction. To ascertain this problem, the following experiments were carried out, using the same apparatus and the same method hitherto employed. To the carbide powder of 900-mesh fineness and 71.3%

(1) T. Aono, This bulletin, **7** (1932), 247.

purity, a definite quantity of each "Darco carbon" (an active carbon), technical calcium cyanamide (21.68% N and 13.3% C) and calcium chloride (previously ignited and dehydrated) was added respectively and subjected to nitrogen at the same temperature (870°C.) and pressure (1 atm.) and the velocity of azotation was compared with the carbide without any added substance. The results are shown in Table 6, Figs. 5 and 6.

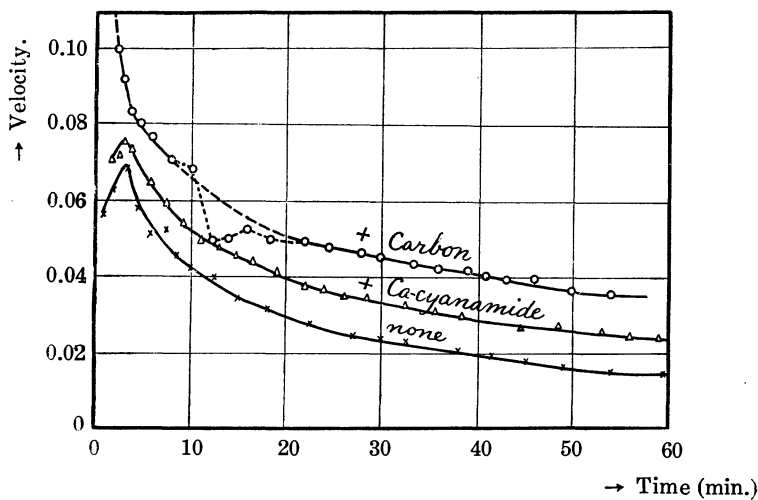


Fig. 5. Azotation velocity of powdered carbide at 870°C. with various catalysers.

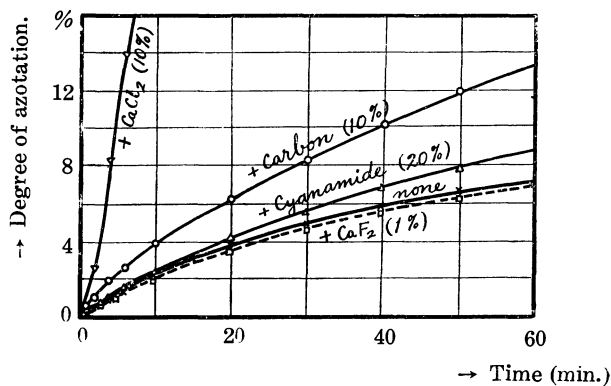


Fig. 6. Effect of various catalysers upon the azotation of powdered carbide at 870°C.

Table 6.

Effect of catalysers on the azotation of carbide power
at 870°C. and 1 atm. pressure.

Exp. No.	524		525		521		523		361**	
Catalyser added %	0		Cyanamide, 20		"Darco C," 10		CaCl ₂ , 10		CaF ₂ , 1	
Sample. gr.	2.7023		2.702+0.543		2.741+0.274		2.736+0.274		4.043	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	0.0567	0.22					0.345	1.09		0.17
2	0.0633	0.46	0.0715	0.50	0.1070	1.10	0.625	2.62	0.0512	0.40
3	0.0690		0.0752	0.78	0.0925		0.835	5.05	0.0530	0.65
4	0.0655	1.02	0.0727	1.06	0.0830	1.91	1.000	8.35	0.0528	0.90
6	0.0520	1.49	0.0640	1.57	0.0770	2.61	0.715	13.90	0.0462	1.37
	0.0470		0.0578	2.03	0.0714		0.600	18.33	0.0396	1.77
10	0.0424	2.28	0.0525	2.45	0.0680	3.89	0.545	22.20	0.0358	2.13
15	0.0345	3.12	0.0456				0.455	30.65	0.0270	2.89
20	0.0298	3.79	0.0400	4.18	0.0500	6.21	0.393	37.78	0.0250	3.53
30	0.0243	4.96	0.0333	5.59	0.0455	8.34	*		0.0208	4.63
40	0.0195	5.92	0.0287	6.82	0.0408	10.17			0.0170	5.58
50	0.0158	6.75	0.0252	7.89	0.0360	11.95			0.0148	6.34
62	0.0142	7.50	0.0230	8.90		13.70			0.0130	7.13
Product N %	powder 2.34		powder 5.8		sintered very slightly 3.72		sintered slightly. >15		powder	

* N₂-pressure was changed after 20 minutes and the change of velocity with pressure was measured. The result was already reported in this bulletin, 7 (1932), 143-154.

** The carbide and the velocity unit are different from the other four; its purity is 68.2%.

It is evident from the table and figures, that addition of an active carbon not only accelerates the reaction, but also almost puts out the maximum point of velocity. In experiment No. 521 the maximum velocity did not appear after two minutes before which the velocity was not measured, while without carbon the maximum velocity appears after more than 3 minutes at this temperature. The accelerating action of carbon, especially at the earlier stage of the azotation may be recognized to be conspicuous. The action of the cyanamide at this lower temperature can also be attributed to the carbon contained in the cyanamide. It should be weak, because its quantity ($13.3 \times 0.2 = 2.66\%$) is small with respect to the carbide, and as the carbon in the cyanamide is in the form of graphite with

some amorphous carbon, and as it had been subjected to higher temperatures, the activity will be but weak. Calcium fluoride had no effect at 870°C., while calcium chloride accelerated the reaction extraordinarily, which will be partly due to the action of decomposing the carbide, and setting carbon free. As to this problem, the discussion will be given later in this bulletin.

The most of these experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co. Ltd. Tokyo, before Sept. 10th (1930), and reported to the meeting of engineers and directors of the Co. on that day.

Summary.

The effects of some catalytic substances to the velocity of azotation of both powdered and "granular" carbide were experimentally determined.

1. There is an optimum quantity of calcium fluoride to be added to the carbide to get the highest velocity of azotation, the quantity of which is a function of both carbide and reaction temperature.

2. The added substances not only have some influence upon the velocity, but also change the characteristics of the velocity curves of azotation.

3. Carbon and carbon containing substances or those which sets carbon free from carbide show strong catalytic action to the azotation of calcium carbide. The opinion that the nascent carbon must be acting as a catalyser is supported.

Research Laboratory of the Denki-Kagaku-Kogyo Co. Ltd.,
Yurakucho, Kojimachi-ku, Tokyo.

THE RELATION BETWEEN KOLBE'S REACTION AND
HYDROGEN ION CONCENTRATION. VII. THE
MECHANISM OF KOLBE'S REACTION.

By Hamilton Ryoichi MATSUDA.

Received July 4th, 1932. Published September 28th, 1932.

The present author's observation on the gas evolved from the solutions of potassium acetate under electrolysis, and the studies on chemical behaviours of the solutions during the electrolysis—especially their oxidizing and reducing actions—led him to the conclusion that ethane in these cases had its origin in acetyl peroxide, as already had been reported in the previous communication.⁽¹⁾

(1) This Bulletin, 7 (1932), 18.

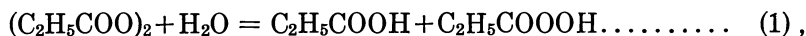
In order to examine the validity of the Peroxide Theory, electrolyses of potassium propionate solutions were carried out under nearly the same principle as in the case of the acetate solutions.

Although there is a report from another source that a highly concentrated solution of sodium propionate acidified with propionic acid produces butane in a larger quantity than ethylene⁽¹⁾ such is to be regarded only as an exceptional case, since ethylene, from a general point of view, may be taken as the principal product of the Kolbe's Reaction of a propionate solution. Because a concentrated solution of potassium propionate produces ethylene in an overwhelming quantity, accompanied by far less amounts of butane and ethyl propionate; and moreover, butane decreases as the concentration of the solution is lowered.⁽²⁾

As a proper sequence the present paper chiefly deals with the relation between the ethylene formation and oxidizing action of the electrolysed solution.

As is mentioned below, propionyl peroxide which can be taken as the original product of the Kolbe's Reaction of potassium propionate just as the acetyl peroxide in the case of potassium acetate, is a substance of a greater stability than the latter,⁽³⁾ hence it follows that propionyl peroxide must be more resistible to the anodic actions than acetyl peroxide. It may be therefore presumed that there is formed, in this case, propionyl peroxide or certain peroxidic substances formed from it by decomposition, in quantities greater than equivalent to the corresponding peroxidic substances produced in the case of potassium acetate, thus giving a stronger oxidizing power to the propionate solution.

As are described below, the experimental facts observed by the author are all in the fullest agreement with this assumption, and exactly as in the case of the acetate, the formation of hydrogen peroxide is explained by assuming that it is produced by the hydrolyses of propionyl peroxide as shown in the following equations :



(1) Zimmermann, Dissertation, Gieszen, 1899.

(2) Petersen, *Z. physik. Chem.*, **33** (1900), 106.

(3) Acetyl peroxide : Nef, *Ann.*, **298** (1897), 289; propionyl peroxide, Clover, Richmond, *Am. Chem. J.*, **29**, 191.

Experimental.

The apparatus used for electrolysis were the same as those mentioned in the preceding papers,⁽¹⁾ 100 c.c. of the electrolyte having been employed each time.

Test for hydrogen peroxide: the presence of this substance was attested by means of a titanium sulphate solution.

Potassium permanganate test: 20 c.c. of the sample solution were acidified with an excess of sulphuric acid, and titrated with n/100 potassium permanganate solution.

Potassium iodide and starch test: 20 c.c. of the sample solution were added to a potassium iodide solution, and iodine that had been set free was titrated with n/100 thiosulphate solution, using a starch solution as the indicator. When reaction was considered to have ceased, a little more potassium iodide was added to ascertain that there was no recovery of the starch-iodine colour.

Table 1.

Electrolyses of dilute solutions of potassium propionate.

Electrolyte % KPr	pH		Duration of Electrolysis	Exam. of the solution			C ₂ H ₄
	orig.	after		H ₂ O ₂	$\frac{n}{100}$ KMnO ₄	KI+Starch	
0.1	6.0	6.0	12 min.	abs.	4 drops*	no reaction	0
0.3	6.1	6.1	7	„	7	„	„
0.5	„	„	12	„	15	„	„
0.7	6.2	6.3	20	„	25	„	„
1.0	„	7.9	30	pres.	70	$\frac{n}{100}$ Na ₂ S ₂ O ₃ 29 drops	6.5%

* 25 drops = 1 c.c.

Current density was 3.6 A/dm.² at the anode in the case of 0.1% solution and 10 A/dm.² in other cases. Temperature ranged 9–12°C., except in the case of 0.3% solution, which was electrolysed at 17–18°C. The gas samples were collected as follows: 35 c.c. from 0.1% solution and 60 c.c. from 0.3% solution, each during the whole course of electrolysis; but from three other solutions 60 c.c. were collected in the first six minutes.

The first four solutions were very similar to one another not only in changing their pH values but very slightly during the electrolysis but in

(1) loc. cit.

producing neither oxidizing substances nor ethylene; only difference being in their respective reducing power against potassium permanganate.

0.1 Per cent. solution was electrolysed by a current of much smaller density than that used in other solutions, that is, 3.6 A/dm². As was observed in the case of acetate⁽¹⁾ a current of greater density makes Kolbe's Reaction more difficult to occur in a very dilute solution. It was presumed by analogy that 0.1% solution of potassium propionate would never produce ethylene, if a current of greater density, such as 10 A/dm²., were applied.

1.0 Per cent. solution differed from others in a remarkable manner in changing its pH value in a far broader range, and in producing some oxidizing substance, perhaps other than hydrogen peroxide, as well as ethylene.

It was thus found that the formation of ethylene by electrolysis of potassium propionate is always accompanied by that of some oxidizing substances, in exact analogy to the facts observed in the case of acetate-electrolysis. It was also discovered that the least necessary concentration of potassium propionate solution capable of undergoing Kolbe's Reaction lies somewhere between 0.7 and 1.0%, when worked under above mentioned conditions.

Table 2.

Electrolyses of dilute potassium propionate solutions, which contained 1 gr. ammonium carbonate per 100 c.c.

$D_A = 15 \text{ A/dm}^2$., Temp. = 8–10°C.

Electrolyte % KPr	pH		Duration of Electrolysis	Exam. of the solution			C ₂ H ₄
	orig.	after		H ₂ O ₂	$\frac{n}{100}$ KMnO ₄	KI+Starch	
0.1	8.5	8.8	5 min.	abs.	4 drops	$\frac{n}{100}$ Na ₂ S ₂ O ₃ 3 drops	0.4%
0.3	„	8.7	10	pres.	18	6	„
0.5	„	„	15	„	36	20	0.6
1.0	„	„	30	„	10.7 c.c.	42	1.2

For analysis, 60 c.c. of the evolved gas were collected, and it took 5 minutes in the case of 0.1% solution, and 3¹/₂–4 minutes after the start of electrolysis in every one of the other cases.

The ethylene production even from such very dilute solutions as shown above was possibly due to the addition of ammonium carbonate which caused

(1) loc. cit.

sufficient lowering of the anodic potential, raising the pH value of the solution, even under a comparatively higher current density such as $D_A = 15 \text{ A/dm}^2$.

0.1 Per cent. solution formed hydrogen peroxide no more, this probably on account of its extreme smallness of concentration. While even the first solution in the above table produced ethylene, 1.0% solution produced it in a much less amount when compared with that evolved from the solution of the same concentration to which no ammonium carbonate was added (compare Tables 1 and 2). This is because the lowering of the anodic potential caused by the presence of ammonium carbonate reached such an extent that the solution became unsuitable for ethylene formation. In this case again, the ethylene formation was found always accompanied by the oxidizing action of the electrolysed solution.

The results of the electrolysis of a solution containing 5.0 gr. potassium propionate and 2.0 gr. propionic acid per 100 c.c. were as follows :

Table 3.

Electrolyte, (5.0 gr. potassium propionate+2.0 gr. propionic acid per 100 c.c.) solution,

$D_A = 15 \text{ A/dm}^2$, Temp. = $8-10^\circ\text{C}$., Original pH = 5.0.

Duration of Electrolysis	Exam. of the solution				C_2H_4
	pH	H_2O_2	KMnO_4	KI+ Starch	
15 min.	5.1	trace	n/100 2.8 c.c.	n/100 $\text{Na}_2\text{S}_2\text{O}_3$ 4 drops	26.6%
30	5.3	„	3.8	11	26.2
45	5.9	pres.	6.0	26	„
1 hours	7.9	„	10.0	5.0 c.c.	27.5
2	8.5	„	51.5	6.5	14.4
3	9.2	„	67.5	11.0	6.2
4	9.3	„	„	17.0	3.4
5	„	„	70.0	25.5	1.7
6	9.2	„	85.0	27.6	0.6
7	„	„	50.0	21.5	0.2
9	9.1	„	32.5	14.5	

The curves in Fig. 1 represent the pH, the thiosulphate and the ethylene values given in Table 3. The values on the ethylene curve corresponding to the durations 0, 1 and $1/6$, $1\frac{1}{2}$, $2\frac{1}{2}$ and $3\frac{1}{2}$ hours are not given in the table.

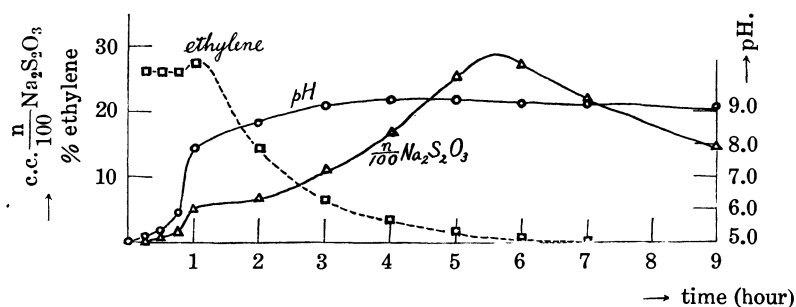


Fig. 1. Electrolyte, (5 gr. KPr + 2 gr. HPr) per 100 c.c.

$D_A = 15 \text{ A/dm}^2$, Temp. = $8-10^\circ\text{C}$.

The ethylene formation was almost constant for the first one hour, when the pH value quickly increased from 5.0 to nearly 8.0. It can be gathered from these facts that during the first hour the concentration of the propionate was always kept constant at the original value at the cost of that of the free acid. After that, the ethylene formation began to decrease, reaching almost nought in six hours, and the pH value, after rising gradually, remained almost constant at 9.3 during the last six hours of the experiment.

The thiosulphate consumption was slight for the first half an hour, the pH value of the solution remaining lower than 5.5; then it promptly and perceptively increased with the rise of the pH value; and at the same time the formation of ethylene was most abundant during this period. After this it increased gradually till at last it reached the maximum value before the ethylene formation finished.

In the case of potassium acetate the relation was entirely different. The thiosulphate consumption was always found greatly depressed by the intense ethane formation, and its maximum value was reached after the ethane formation had ceased.

In this case the presence of hydrogen peroxide was traced after 15 minutes' electrolysis, when the pH value was as low as 5.1. Its actual presence, however, became quite distinct 30 minutes later, when the pH value was 5.9. This also was entirely different in the case of above mentioned acetate solution, in which hydrogen peroxide was not detected even after 45 minutes' electrolysis, when the pH value was found to be 5.9.

The potassium permanganate consumption quickly increased throughout the second and third hours of the electrolysis. This fact indicates the gradual increase of the formation of reducing substances, chiefly caused by the rise of the pH value from 8.0 to 9.2.

The content of butane in the gas samples ranged from 0.2 to 0.6 volume %; the presence of ester in the electrolysed solution could distinctly be detected by its sweet smell. But these two substances can not be considered to play an important rôle in this electrolysis.

If the formation of ethylene is assumed to be due to the decomposition of propionic peracid according to the following equation :



the decomposition reactions must be regarded to proceed in two ways, one, according to the equation (3), and the other, according to the equation (2), and these two reactions to take place side by side, to a certain extent, at the pH value ranging 8.0–9.3, and the former decomposition steadily to decline with the progress of electrolysis in contrast to the predominance of the latter.

The results of the electrolysis of a solution containing 5.0 gr. potassium propionate and 5.0 gr. ammonium carbonate per 100 c.c. are given in the following table and figure :

Table 4.

Electrolyte, (5.0 gr. potassium propionate + 5.0 gr. ammonium carbonate per 100 c.c.) solution,

$D_A = 15 \text{ A/dm}^2$, Temp. = 6–7°C., Original pH = 8.7.

Duration of Electrolysis	Exam. of the solution				C_2H_4	O_2
	pH	H_2O_2	$\frac{n}{100} \text{ KMnO}_4$	KI + Starch		
0 hour					14.8%	8.6%
1					14.2	
2	9.0	pres.	35.0 c.c.	$\frac{n}{100} \text{ Na}_2\text{S}_2\text{O}_3$ 2.7 c.c.	10.2	6.2
3					4.6	
4	8.6	pres.	41.0	7.5	3.2	8.0
6	8.5	,,	45.0	8.5	0.8	
8	8.0	,,	17.0	7.1	0.4	13.8

As no small amounts of oxygen were observed to be evolved, the internal oxidation in this solution must be taken as rather insignificant (compare with the corresponding case of the acetate, Table 7 in the previous paper, loc. cit.). The comparatively smaller values of potassium permanganate consumption conforms to this conjecture.

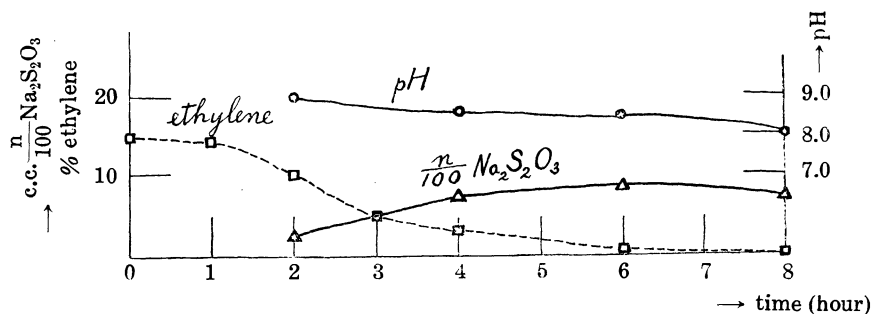


Fig. 2. Electrolyte, (5 gr. KPr+5 gr. amm. carbonate) per 100 c.c.
 $D_A = 15 \text{ A/dm}^2$, Temp. = 7°C .

The higher value of pH, and, consequently, a lower anodic potential, caused by the addition of ammonium carbonate acted unfavourably to the discharge of propionyl ion, $\text{C}_2\text{H}_5\text{COO}^-$, as indicated by the above fact, as well as by the fact that the maximum values showing the ethylene formation and thiosulphate consumption were both remarkably lower than those given in Table 3.

Hydrogen peroxide may be regarded in the present case to have been formed soon after the start of electrolysis for the reason of the higher value of pH. The coincidence between the declination of the ethylene formation and the ascendancy of the thiosulphate consumption was very clearly observed: a fact which, the author is confident, amply justifies this Peroxide Theory.

In closing this seventh paper on these researches, let the author express once more his most profound thankfulness for the constant encouragement and ever helpful suggestions, which he has received throughout his somewhat prolonged studies from his old master, Professor Dr. M. Matsui of Kyoto Imperial University.

Summary.

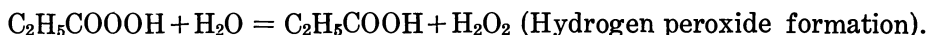
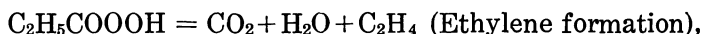
(1) 0.1–0.7 Per cent. solution of potassium propionate gave neither ethylene nor signs that the solution had undergone any oxidation, when electrolysed by passing a current of $D_A = 10 \text{ A/dm}^2$ at $9\text{--}12^\circ\text{C}$.

(2) When 1.0% potassium propionate solution was electrolysed under the same conditions, ethylene was produced, and at the same time oxidizing action of the solution became observable. Hydrogen peroxide was also found present.

(3) The presence of ammonium carbonate proved so effective as to produce ethylene even from the most dilute solution. Ethylene formation was always accompanied by oxidizing action of solutions in all cases alike.

(4) Electrolyses of a solution containing 5.0 gr. potassium propionate and 2.0 gr. propionic acid and the one containing 5.0 gr. potassium propionate and as much ammonium carbonate, each in 100 c.c., were investigated.

(5) The assumption of propionyl peroxide at the intermediate product provides a very satisfactory explanation of Kolbe's Reaction and also of other reaction related to it in the electrolysis of a propionate; the production of ethylene, hydrogen peroxide and similar oxidizing substances may all be explained to take place according to the following scheme:



(6) The difference observed between electrolyses of potassium propionate and potassium acetate will easily be understood, if we take notice of the higher stability of propionyl peroxide in comparison with acetyl peroxide.

Tokushima Technical College,
Tokushima.

X-RAY STUDY ON THE ELECTROLYTIC Fe-Ni ALLOYS.

By Keizô IWASE and Nobuyuki NASU.

Received August 15th, 1932. Published September 28th, 1932.

Synopsis.

Iron and nickel were co-deposited in various proportions electrolytically from their mixed sulphate solutions, and X-ray diffraction patterns were photographed by the Debye-Scherrer and Seemann-Bohlin methods, and the lattice constants were measured by choosing lines of copper as a standard which was mixed with the alloys in the form of powder. The results obtained were as follows. (1) Iron and nickel in the deposit appears as solid solution. The homogeneity of the solid solution thus formed seems not so good as that of the alloy solidified from the melt. (2) The co-existence of α and γ solid solutions is also observed in the deposits the concentration of which ranged from 14% Ni to 58% Ni. In the alloys solidified from the melt this ranges from 25% Ni to 33% Ni. (3) Lattice constant of α or γ solid solution increases slightly at first, reaches maximum and then decreases as the constant of Ni or Fe increases respectively. From these results it has been concluded that when the total or local concentration of the one metal in the deposit is small, two cases may arise either the metal is forced to deposit among the crystal of the other metal without forming its proper crystal lattice forming

pseudo solid solution as a result of the unit mass of the deposited crystal of that metal is small and consequently it easily diffuses into the other after the deposition. This is the reason why the lattice constant-concentration curve runs upward. But when the concentration is fairly large, the unit mass of that crystal also becomes larger and its diffusion into the other takes place not so easily as before leaving some of that crystal undiffused. This tendency becomes greater as the concentration of that metal increases. The existence of the maximum point on the curve above mentioned and the coexistence of α and γ solid solutions in a wider range of the composition of the deposited alloy are explained sufficiently by the process of deposition above supposed.

Introduction.

There is a few study on the crystal structure of the alloy⁽¹⁾ electrolytically co-deposited from the aqueous solution of the salts of two kinds of metal. Nakamura⁽²⁾ observed by the X-ray study that the crystal of the electrolytic brass containing 17.52% of Zn co-deposited from the cyanide solution well coincides with the alloy of the same composition obtained from the melt in its form and in its lattice constant. G. Fuseya and K. Sasaki⁽³⁾ also concluded by the X-ray study that the electrolytic Fe-Cr alloy containing 30% of Cr forms solid solution. As to the mechanism of these phenomena the following cases may be considered.

(1) The discharge of the two kinds of metal ion occurs at the position of each inherent crystal lattice, and not at the position of the crystal lattice of their solid solution. But as the state of mixing of the two metals in the deposit is very intimate, two metals easily diffuse with each other and form solid solution.⁽⁴⁾

(2) The discharge of the two kinds of metal ion occurs at the position of the crystal lattice of their solid solution, and not at the position of each inherent crystal lattice when the condition of electrolysis is suitable.

(3) The two kinds of metal ion are forced to discharge at random without being allowed to choose the mode of discharge (1) or (2), and consequently the pseudo solid solution are formed the predominated metal being the solvent. In this case diffusion naturally occurs after the deposition.

By the case of brass or Fe-Cr alloy mentioned above, it is not convenient to decide which is the chief mechanism of deposition among the above three processes, because though Cu and Zn have different crystal forms they diffuse very easily with each other,⁽⁵⁾ and though Fe and Cr do

(1) Electrolytic alloy means a mixture of two or more metals co-deposited by electrolysis.

(2) M. Nakamura, *Bul. Inst. Phys. Chem. Research, Japan, (Riken-Ihō)*, **4** (1925), 71.

(3) G. Fuseya and K. Sasaki, *J. Soc. Chem. Ind., Japan, (Kōgyō-Kagaku-kaiishi)*, **33** (1930), 1337.

(4), (5) Tammann, *Lehrbuch der Metallographie*, 3 Auflage (1923), 233.

not diffuse so easily as the case of Cu and Zn, they have the same crystal form and the difference between the lattice constants is very small being 0.017 Å. So we have chosen the alloys of Fe and Ni to study the mechanism of deposition, and we have prepared a series of the alloy whose composition varies from 0~100% of Ni and studied their structure by the X-ray analysis. In the alloy of this system obtained from the melt up to 25% of Ni, the alloy consists of α solid solution only (body centred cubic lattice) and from 33% of Ni to 100% of Ni only of γ solid solution (face centred cubic lattice) and between 25% and 33% of Ni it consists of α and γ solid solutions (both body centred and face centred).⁽¹⁾

Experimental.

Preparation of Electrolytic Fe-Ni Alloys. Co-deposition of iron and nickel by electrolysis was studied by S. Glasstone and T. E. Symes.⁽²⁾ Using the chemical analysis, the composition of the alloys, prepared by the electrolysis from the mixed sulphate solution of various concentration, were determined. But whether this so called alloy was the true alloy having a definite crystal structure or not was not studied. L. E. Stout and J. Carol⁽³⁾ studied the co-deposition of iron and nickel from their mixed cyanide solution, but they also did not touch the problem of the crystal structure of the deposit. For the present study, the sulphate solution was taken as the electrolyte, the total concentration of which was two normal, and to prevent the formation of ferric hydroxide in consequence of the anodic oxidation during electrolysis the electrolyte was acidified to two normal with sulphuric acid. Glasstone observed that when electrolyte is dilute in its concentration and not stirred during electrolysis for a long time, the iron contents in the deposit more or less decreases though the hydrogen ion concentration does not affect the composition of the deposit. In our experiment, electrolyte was sufficiently concentrated and stirred and in addition to these, our deposit was little in quantity compared with the total metal content in the electrolyte (total metal content 28 gr., deposit about 0.2 gr.), and so the inequality of concentration in deposit may be negligible. As the cathode thin plate of copper, 0.17 mm. in thickness and 20 cm². in effective area, was used and as the anode two thin plates of platinum, 3.5 cm. long and 1.5 cm. wide, were put on either side of the cathode. Electrolysis was carried out at room temperature, and C.D. was always kept at 0.02 amp/cm².

(1) A. Osawa, *Kinzoku-no-Kenkyu*, **2** (1925), 809; T. Kasé, *ibid.*, **1** (1924), 1215.

(2) S. Glasstone and T. E. Symes, *Trans. Faraday Soc.*, **23** (1927), 213; **24** (1928), 370.

(3) L. E. Stout and J. Carol, *J. Am. Electrochem. Soc.*, 1930, Sept. Meeting; *Stahl u. Eisen*, **50** (1930), 1533.

electrolyte being stirred during it. Before electrolysis cathodes were well polished, washed with concentrated KOH solution, dipped in concentrated nitric acid for a few seconds, washed well with water, dipped in dilute sulphuric acid, washed with water again and then used. The volume of electrolyte was 500 c.c., the time of electrolysis 4 hours. After the electrolysis the deposit was separated from the cathode, powdered, and the one half of it was used for X-ray analysis, the other for chemical analysis and the results obtained were as follows.

Table 1.

No.	Concentration of Nickel in	
	Solution (%)	Deposit (%)
1	0	0
2	33	9
3	51	11
4	61	14
5	67	20
6	84	31
7	89	37
8	98	58
9	99	80
10	100	100

X-ray Analysis. The X-ray analysis of the above 10 specimens has been carried out by Debye-Scherrer and Seemann-Bohlin methods. The results are tabulated in Table 2, and graphically represented in Fig. 1. Some of the diffraction patterns taken by the method of Debye-Scherrer are shown in Photo. 1 as examples.

Table 2. Results of X-ray Analysis.

(a) Body-centred Lattice.

No.	% Ni	R	$h_1h_2h_3$	r	$2b$	θ (Radian)	$\sin \theta$	d	$\text{\AA}$
1	0	27.754	211	0.263	108.629	0.977036	0.82884	1.166932	2.858 ₄
1'	0	27.705	„	0.288	108.522	0.977640	0.82918	1.166456	2.857 ₂
2	9	27.754	„	0.275	108.739	0.976320	0.82844	1.167496	2.859 ₇
3	11	27.800	„	0.288	108.456	0.975234	0.82783	1.168354	2.861 ₈
4	14	27.660	„	0.385	108.130	0.975137	0.82776	1.168454	2.862 ₁
5	20	27.727	„	0.238	108.345	0.977554	0.82801	1.168101	2.861 ₂
6	31	27.736	„	0.310	108.620	0.977312	0.82899	1.166720	2.857 ₈
7	37	27.660	„	0.325	108.600	0.979745	0.83033	1.164838	2.853 ₃
8	58	27.721	„	0.280	108.789	0.979540	0.83023	1.164972	2.853 ₆

(b) Face-centred Lattice.

No.	% Ni	R	$h_1h_2h_3$	r	$2b$	θ (Radian)	$\sin \theta$	d	$\text{\AA}$
4	14	27.735	220	0.385	98.478	0.887666	0.77560	1.24703	3.527 ₁
5	20	27.744	„	0.238	98.702	0.887690	0.77562	1.24701	3.527 ₃
6	31	27.742	„	0.310	98.530	0.885688	0.77436	1.24903	3.532 ₈
7	37	27.652	„	0.325	98.420	0.887470	0.77549	1.24721	3.527 ₆
8	58	27.698	„	0.280	98.140	0.883782	0.77315	1.25099	3.538 ₂
9	80	27.679	„	0.295	97.632	0.880756	0.77122	1.25411	3.545 ₁
10	100	27.743	„	0.280	98.912	0.889344	0.77666	1.24534	3.522 ₃
10'	100	27.707	„	0.283	98.834	0.889740	0.77691	1.24499	5.521 ₂

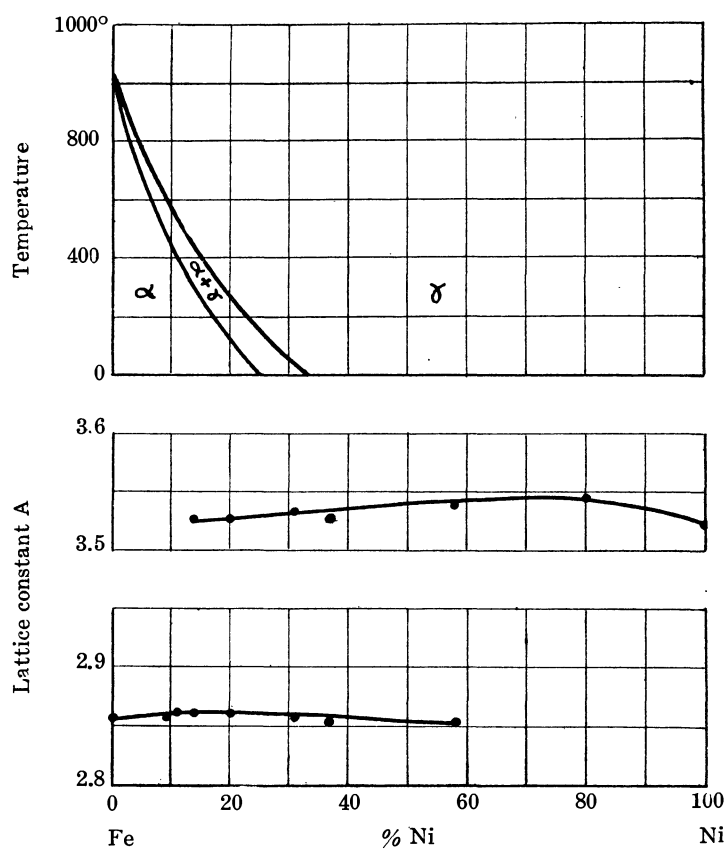


Fig. 1.

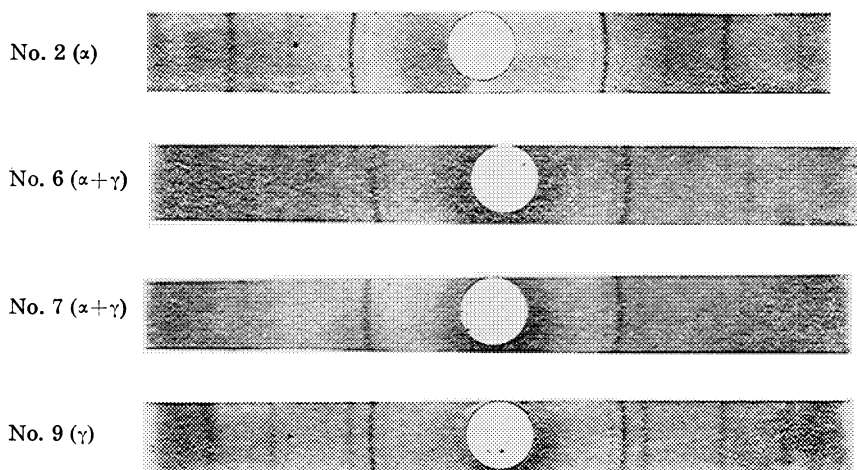


Photo. 1.

Lines in No. 2 consist of those which belong to body centred cubic lattice, lines in No. 9 consist of those which belong to face centred cubic, and in Nos. 6 and 7 we find the mixture of lines of both crystals. Lines of body centred cubic are deeper than those of face centred cubic in No. 6 and opposite in No. 7. This is due to the relative quantity of both crystals. In No. 6 and No. 7 K_{α} lines diffracted from the crystal plane 110 overwrap with those from the plane 111 and seem very thick and deep. To calculate the lattice constants we photographed the lines from pure Cu crystal at the same time on the same film by mixing the fine powder of Cu with the samples. As the lattice constant of Cu is known, effective radius of camera is calculated from the lines of Cu thus photographed and the lattice constants of the samples were calculated therefrom, thus avoiding the errors caused by camera, film etc. On calculating lattice constants we chose 211 K_{α} in the case of body centred cubic lattice and 220 K_{α} in the case of face centred cubic as these lines were relatively thick and not so diffused as others and their reflecting angles are large. For the former line, i.e. 211 K_{α} of body centred lattice, 220 K_{α} and 311 K_{α} lines of Cu are taken as a standard and for the latter line, i.e. 220 K_{α} of face centred lattice, 220 K_{α} line of Cu as a standard adopting for the lattice constant of Cu 3.603 Å.⁽¹⁾ The wavelength of X-ray was calculated as 1.9344 Å from two K_{α} lines by proportion of their intensity. The formula $-r(1+2\cos\theta)$ was used for the correction of the radius of the samples, where r meant the radius of the sample, θ

(1) Int. Crit. Tab., I, 340.

the reflecting angle, because this formula had been used in calculation of the effective radius of the camera from the lines of copper. Care was taken to measure $2b$ because the diffusion of lines caused by electrolysis was great. The lattice constants of the samples are shown in the above table in which R shows the effective radius calculated from the line of copper, the wave-length of X-ray was enacted as $1.9344 \text{ \AA}$. In this table samples No. 1' and No. 10' were heated in vacuum at 600°C for 30 minutes, and others not heated.

Fig. 1 shows these results graphically. The lower part of it shows the lattice constant-concentration curve, and the upper part the equilibrium diagram of the alloy cooled from the melt.⁽¹⁾

Interpretation of the Results.

1. **Lattice Constants of the Electrolytic Metals and Alloys.** The values of lattice constant for iron and nickel found in literature (Table 3) coincide well with ours.

Table 3.

Metal	Fe	Ni
A	2.855 ~ 2.859 ⁽²⁾	3.540 ⁽⁴⁾
		3.514 ⁽⁵⁾
	2.855 ~ 2.856 ⁽³⁾	3.514 ⁽⁶⁾

As iron and nickel electrolyzed contain much hydrogen their lattices expand about $0.001 \text{ \AA}$ as shown in the previous table. For the iron our result agrees well with other, while for the nickel our value is intermediate one among theirs. As for the lattice constants of the alloys made from the melt, we can find several studies by X-ray analysis⁽⁷⁾ but their results don't

(1) A. Ôsawa, T. Kasé, see before.

(2) W. H. Day, *Phys. Rev.*, **25** (1925), 755. Fe_2O_3 was reduced with hydrogen.

(3) A. O. Jung, *Z. Krist.*, **65** (1927), 311. Iron was used which was prepared at Bureau of Standard, the purity of which was 99.937%.

(4) A. W. Hull, *Phys. Rev.*, **17** (1921), 579. Electrolytic nickel was used.

(5) The same with (2).

(6) L. W. McKeehan, *Phys. Rev.*, **21** (1923), 402. Mond nickel the purity of which was 99.7% was used.

(7) M. R. Andrews, *Phys. Rev.*, **17** (1921), 261; **18** (1921), 245; A. Ôsawa, *Kinzoku-no-Kenkyu*, **2** (1925), 809; A. O. Jung, see before; L. W. McKeehan, see before.

coincide with. However all of these studies coincide well with the point that their lattice constants increase in α or γ solid solution as nickel or iron content increases respectively. Contrary to this in our results lattice constants increase at first as the solute increases in its concentration, reach maximum values, and then decrease in both α and γ solid solutions. This is a remarkable difference between their cases and ours. In our preliminary experiment the same phenomena was observed with the two samples containing 42% Ni and containing 58% Ni respectively, which is shown in Fig. 2 (C, D). In this figure the intensity curves are taken with

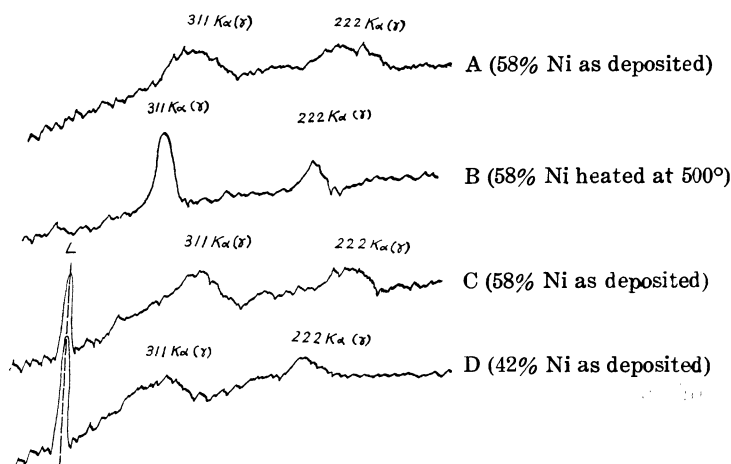


Fig. 2.

the spectral lines corresponding to the two kinds of samples above mentioned, taken on the same film. L means a line marked on the film for taking the intensity curve.

2. Diffusion of Spectral Lines of Electrolytic Alloys. It is observed that though lattice of electrolytic iron and nickel expand owing to the hydrogen, their spectral lines are not diffused so much. But in the case of Fe-Ni alloys deposited they are diffused remarkably, which seems to be due to the smallness, internal stress, and inequality of the composition etc.⁽¹⁾ Fig. 2 (A, B) represents the intensity curves of such lines as examples photographed by Seemann-Bohlin method. In the figure A corresponds to the sample No. 8 as electrolyzed while B corresponds to the same sample heated at 500°C. for 5 hours. As seen in the figure spectral line of B is

(1) R. Brill, *Z. Metalk.*, **75** (1930), 217.

remarkably sharper than that of A. The diffusion of the spectral lines of electrolytic alloys is also seen in Fig. 2 (C, D.).

3. Coexistence of α and γ Phases in a Wide Range. As seen in Fig. 1 the range in which α and γ solid solutions of usual alloy coexist lies between 25 and 33% of Ni, but in the electrolytic alloy this ranges from 14% to 58% of Ni. This is a second difference between the two kinds of alloys one of them deposited electrolytically and others solidified from the melt throwing a certain clue to the interpretation of the mechanism of deposition of the two metal ions.

4. Mechanism of Deposition of the Alloy. From the results of experiment explained above it may be concluded that the mechanism (2) that is, the deposition of two kinds of ions takes place at the position corresponding to their solid solution can not be supported in the case of iron and nickel deposited from sulphate solution. The results of our experiment can satisfactorily be explained by assuming that principally the mechanism (1) governs the deposition and in some cases may the mechanism (3) will also play some part, i.e. ions possibly be compelled to discharge without chance to choose the definite position. By these mechanism the results of experiment are satisfactorily explained as follows, taking the α solid solution for example. Though Fe and Ni crystallize individually, when the concentration of nickel in the deposit is small, the number of nickel atoms contained in the single nickel crystal is small, so that the diffusion of this nickel crystal into the surrounding iron crystal after the deposition can easily take place making α solid solution.

When the concentration of nickel in the deposit increases, number of atoms of nickel in single crystal and the concentration of such crystal in the deposit also increases, so the concentration of nickel in the α solid solution formed by the diffusion of nickel atoms may increase and the lattice constant increases as a result. At the same time it becomes more and more difficult to diffuse all of the Ni crystal as the latter becomes large, and thus some of nickel atoms remain undiffused. In the next step as the concentration of nickel increases, this undiffused nickel crystals may become large. Into these crystals iron atoms will be mixed by the mechanism (3). Thus γ solid solution forms.

When the concentration of nickel increases again diffusion of nickel atom into the lattice of iron decreases on the contrary, but the crystal of nickel undiffused increases, and the concentration of nickel in the body centred cubic lattice decreases. At the same time, the concentration of iron in γ solid solution increases, and the lattice constant of it also increases.

Thus lattice constant-concentration curve has maxima and the heterogeneous region of α and γ solid solution appears to be very wide having no connection with the diagram of the alloy formed from melt. And thus that one of the causes of the enormous diffusion of spectral lines of these electrolytic alloy is based upon the inhomogeneity of concentration in the solid solution seems to be possible when such a mechanism is considered.

In conclusion present writers express their hearty thanks to Dr. S. Sekito and Mr. Z. Nishiyama who kindly photographed X-ray spectral lines.

Summary.

1. Iron and nickel were co-deposited from their acidic mixed sulphate solution, and the diffraction patterns were photographed by various samples containing from 0 to 100% of nickel.

2. α and γ solid solution were observed in each sample and neither pure iron nor nickel could be found.

3. The heterogeneous region of α and γ was enormously wide compared with the alloy formed from the melt.

4. The lattice constant-concentration curve has maxima in α and γ solid solution.

5. The spectral lines of the solid solution was remarkably diffused. From these results it has been concluded that these two metals principally discharge at the position of each individual crystal lattice and in some cases discharge having no chance to choose such positions may occur, but they don't discharge at the position of the crystal lattice of solid solution of these two metals in the case experimented.

The Research Institute for Iron, Steel and Other Metals.
Tohoku Imperial University, Sendai.

TWO IRON NITRIDES.

By Shun-ichi SATOH.

Received August 13th, 1932. Published October 28th, 1932.

I. Introduction. Compounds of iron and nitrogen, so far as is known in literature, are $\text{Fe}_{12}\text{N}^{(1)}$, $\text{Fe}_8\text{N}^{(2)}$, $\text{Fe}_6\text{N}^{(2)}$, $\text{Fe}_4\text{N}^{(3)}$, $\text{Fe}_7\text{N}_2^{(4)}$, $\text{Fe}_6\text{N}_2^{(4)}$, $\text{Fe}_5\text{N}_2^{(5)}$, $\text{Fe}_2\text{N}^{(6)}$, $\text{Fe}_3\text{N}_2^{(7)}$ and $\text{FeN}^{(8)}$. Of these, Fe_4N and Fe_2N are definitely known compounds. Fe_2N is obtained by passing gaseous ammonia over iron powder at 450°C . It is a paramagnetic substance⁽¹⁰⁾ forming a hexagonal close packed lattice⁽⁹⁾. Its heat of formation is 3040 cal.⁽¹¹⁾ Fe_4N is obtained by heating Fe_2N in vacuo at $440^\circ\text{--}550^\circ\text{C}$. It forms a face centred cubic lattice⁽¹²⁾, being a ferromagnetic substance⁽¹⁰⁾. Its heat of formation is not yet determined. The equilibrium diagram of iron and nitrogen system was studied by C. B. Sawyer⁽¹³⁾ (thermal analyses), T. Murakami and S. Iwaizumi⁽¹⁴⁾ (magnetic analyses), A. Fry⁽¹⁰⁾ (microscope and magnetic analyses) and by E. Lehrer⁽¹⁵⁾ (magnetic analyses and X-ray). Fig. 1 shows a most reliable equilibrium diagram obtained by E. Lehrer⁽¹⁵⁾.

The equilibrium between iron, iron nitride, ammonia and hydrogen at a high temperature was studied by E. Baur and G. L. Voerman⁽¹⁶⁾, A. A. Noyes

-
- (1) N. Tschischewski, *J. Iron and Steel Inst.*, **92** (1915), 77.
 - (2) A. A. Noyes and L. B. Smith, *J. Am. Chem. Soc.*, **43** (1921), 480.
 - (3) C. Charpy et L. Bonnerot, *Compt. rend.*, **158** (1914), 996; A. Fry, *Stahl und Eisen*, **43** (1923), 1272.
 - (4) A. W. F. Rogstadius, Dissertation Upsala, (1860).
 - (5) H. Braune, *Stahl und Eisen*, **26** (1906), 1360.
 - (6) G. J. Fowler, *J. Chem. Soc.*, **79** (1901), 288.
 - (7) A. H. White and L. Kirschbraun, *J. Am. Chem. Soc.*, **28** (1906), 1347.
 - (8) A. Guntz, *Compt. rend.*, **135** (1902), 739.
 - (9) G. Hägg, *Nova acta regiae societates scientiarum Upsaliensis*, IV, **7**, No. 1; A. Osawa and S. Iwaizumi, *Z. Kryst.*, **69** (1928), 26.
 - (10) A. Fry, loc. cit.
 - (11) G. Fowler, Ph. J. Hartog, *J. Chem. Soc.*, **79** (1901), 299.
 - (12) R. Brill, *Naturw.*, **16** (1928), 593; A. Osawa and S. Iwaizumi, loc. cit.; O. Eisenhut und E. Kaupp, *Z. Elektrochem.*, **36** (1930), 392. G. Hägg, loc. cit.
 - (13) C. B. Sawyer, *Trans. Am. Inst. Min. Met. Eng.*, **69** (1923), 810.
 - (14) T. Murakami and S. Iwaizumi, *Kinzoku no Kenkyu*, **5** (1928), 159.
 - (15) E. Lehrer, *Z. Elektrochem.*, **36** (1930), 460.
 - (16) E. Baur und G. L. Voerman, *Z. physik. Chem.*, **52** (1905), 471.

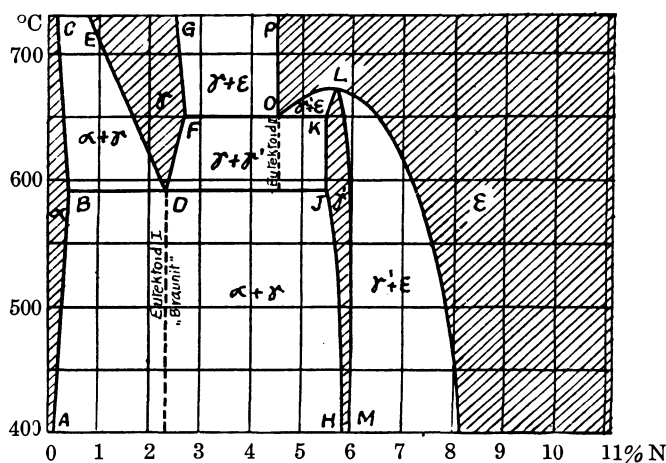


Fig. 1.

Equilibrium diagram of iron and nitrogen according to E. Lehrer.

and L.B. Smith⁽¹⁾, E. Lehrer⁽²⁾, P. H. Emmett, S.B. Hendricks, S. Brunauer⁽³⁾ and S. Brunauer, M. E. Jefferson, P. H. Emmett, S. B. Hendricks⁽⁴⁾. The authors of the first two papers did not clearly determine the composition of the solid phase that takes part in equilibrium, but E. Lehrer⁽²⁾ determined that Fe_2N and Fe_4N as well as Fe_4N and Fe could coexist but Fe and Fe_2N could not coexist to take part in equilibrium.

The author measured the heat of formation of Fe_4N by means of calorimeter. Then he obtained the equilibrium equations of the systems iron, iron nitrides, ammonia and hydrogen from the observed heat of formation of Fe_4N and compared them with the experimental data obtained at high temperatures. Next, he studied the electrochemical properties of iron nitrides.

II. Specimens. The author prepared iron nitride with the apparatus shown in one of his previous papers⁽⁵⁾ as Fig. 1. Iron oxide, which he obtained by igniting iron oxalate, was reduced with electrolytic hydrogen. Pure iron thus obtained was treated with gaseous ammonia at 450°C . for 40 hrs. Gaseous ammonia was obtained by evaporating liquid ammonia; it was purified through solid potassium hydroxide, calcium oxide, barium

(1) A. A. Noyes and L. B. Smith, loc. cit.

(2) E. Lehrer, *Z. Elektrochem.*, **36** (1930), 388.

(3) P. H. Emmett and others, *J. Am. Chem. Soc.*, **52** (1930), 1456.

(4) S. Brunauer and others, *J. Am. Chem. Soc.*, **53** (1931), 1778.

(5) S. Satoh, this Bulletin, **5** (1930), 291.

oxide and molten metallic sodium. Iron nitride which was produced in this way, contains 10.65% nitrogen; it is paramagnetic substance and called ϵ . Then he decomposed ϵ in vacuo at 500°C., at which Fe_4N does not decompose, and obtained nitrides which contain respectively 6.15% and 6.53% nitrogen and which are called $\epsilon + \gamma'$. Next, he decomposed $\epsilon + \gamma'$ in vacuo at 550°C., at which Fe_2N decomposes, and obtained nitride, containing 5.52% nitrogen, which is called $\gamma' + \alpha$. The decomposition was carried out by means of the apparatus referred to as Fig. 2 in the previous paper⁽¹⁾. Iron nitride which contains 6.53% nitrogen was used in the calorimetric investigation; the other nitrides were used to study their electrochemical properties.

The author analysed the nitrides, employing the method adopted by F. Wüst and J. Duhr⁽²⁾. A fused silica tube specially made was used for distillation to prevent yielding alkalis in the distillate. By analysing oft-sublimated ammonium chloride, reliable results were obtained. The apparatus is shown in Fig. 2.

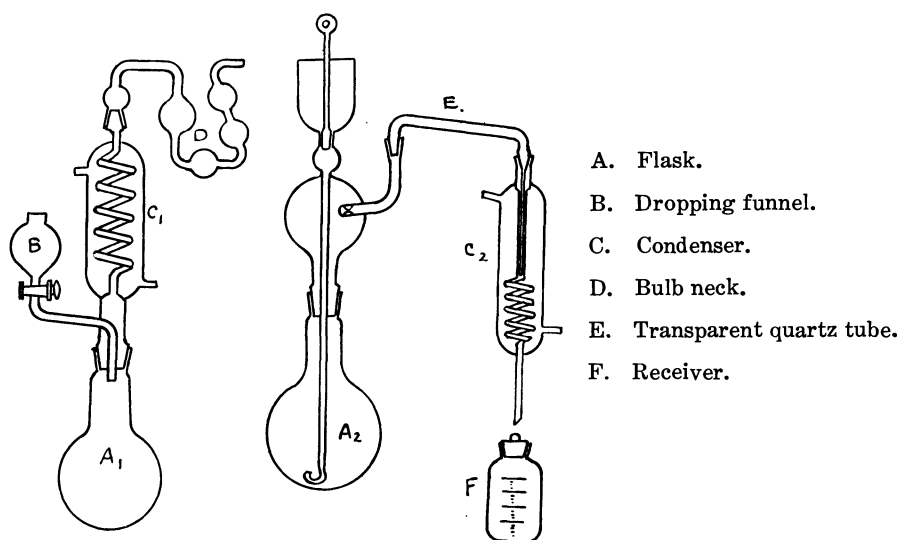


Fig. 2. Apparatus used for analysis of nitrogen in iron.

The powder photographs were taken with two cameras, diameters of which were respectively 60.1 and 60.4 mm. Fe-K-radiation was used from a tube of Siegbahn type, which was run with about 30,000 volts and 4 milli-

(1) S. Satoh, this Bulletin, **5** (1930), 291.

(2) F. Wüst und J. Duhr, *Mitt. Kaiser Wilhelm Inst. Eisen fors.*, **2** (1921), 39.

amperes, Powder photograms are indicated in Fig. 3. The $\sin^2\theta$ values which the author has obtained from the photograms, using Hadding's correction :

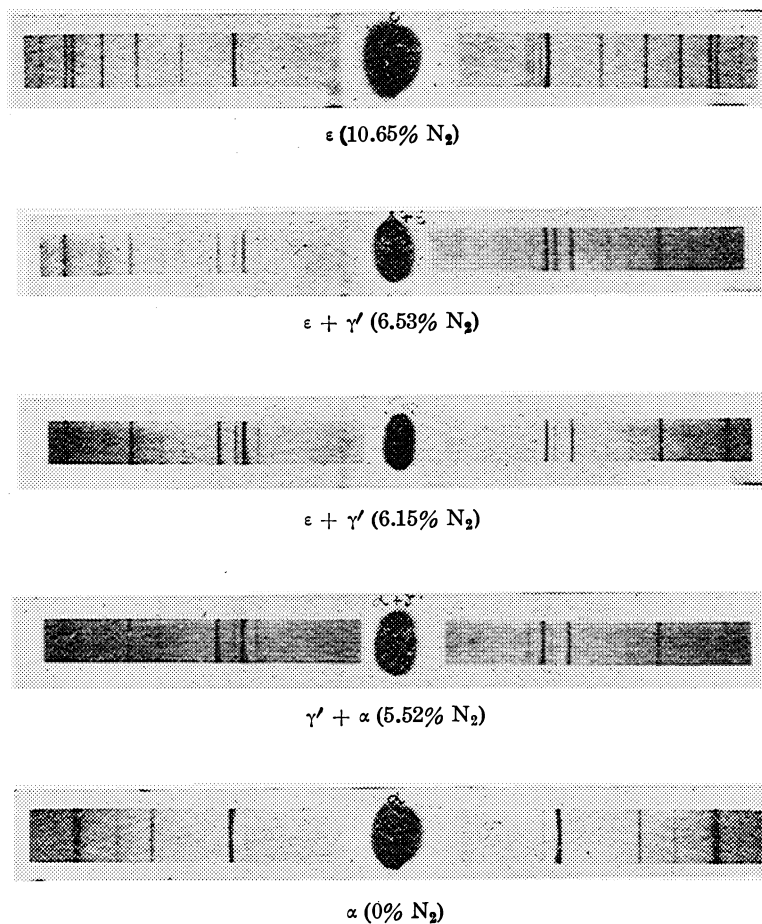


Fig. 3. Powder photograms of iron nitrides.
Fe-K-radiation.

$$2\gamma_{\text{corr.}} = 2\gamma_0 - \rho(1 \pm \cos 2\theta)$$

are given in Tables 1-5, together with the calculated values. The calculated values of $\sin^2\theta$ in Table 1 were obtained by the formula :

Table 1. Powder photograms of iron nitride (ϵ) (10.65% N_2).
Fe-K-radiation.

Film dia. 60.4 mm.

Intensity	Radiation	$h k l$.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
St.	α	100	0.1622	0.1626	Hex.
M.	β	101	0.1728	0.1731	"
St.	α	002	0.1908	0.1914	"
St.	α	101	0.2101	0.2105	"
W.	β	102	0.2905	0.2911	"
St.	α	102	0.3527	0.3540	"
W.	β	110	0.4009	0.4011	"
St.	α	110	0.4866	0.4878	"
St.	α	103	0.5917	0.5932	"
W.	α	200	0.6487	0.6504	"
St.	α	112	0.6767	0.6791	"
St.	α	201	0.6967	0.6982	"
W.	α	004	0.7623	0.7655	"

$$\sin^2\theta = \frac{\lambda^2}{4} \left[\frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right]$$

where λ is the wave-length of the iron radiation — $K_\alpha = 1.932 \text{ \AA}$. and $K_\beta = 1.753 \text{ \AA}$; a and c are elementary dimensions — $a = 2.767 \text{ \AA}$. and $c = 4.417 \text{ \AA}$. The calculated values of $\sin^2\theta$ of ϵ -phase in Tables 2 and 3 were obtained by the above formula where $a = 2.713 \text{ \AA}$. and $c = 4.376 \text{ \AA}$. The calculated values of $\sin^2\theta$ of γ' -phase in Tables 3 and 4 were obtained by the formula:

Table 2. Powder photograms of iron nitride ($\gamma' + \epsilon$) (6.53% N_2).
Fe-K-radiation.

Film dia. 60.4 mm.

Intensity	Radiation.	$h k l$.	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
W.	β	111	0.1599	0.1606	F. C. C.
v. w.	α	100	0.1689	0.1691	Hex.
v. w.	β	101	0.1817	0.1792	"
St.	α	111	0.1940	0.1952	F. C. C.
St.	β	200	0.2185	0.2141	"
St.	α	200	0.2607	0.2603	"
M.	α	102	0.3644	0.3641	Hex.
W.	β	220	0.4273	0.4282	F. C. C.
W.	α	110	0.5084	0.5073	Hex.
St.	α	220	0.5212	0.5206	F. C. C.
W.	β	311	0.5868	0.5888	"
M.	α	103	0.6094	0.6079	Hex.
W.	α	112	0.7029	0.7023	"
St.	α	311	0.7134	0.7146	F. C. C.
W.	α	201	0.7252	0.7252	Hex.
St.	α	222	0.7796	0.7795	F. C. C.

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) .$$

where the side of elementary cube a is 3.789 Å. The calculated values of $\sin^2\theta$ of pure iron in Table 5 were obtained by the above formula where $a = 2.86$ Å. The accordance between the observed and calculated values of

Table 3.
Powder photograms of iron nitride ($\gamma' + \epsilon$) (6.15% N₂)
Fe-K-radiation.

Film dia. 60.1 mm.

Intensity	Radiation	$h\ k\ l$	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Lattice
W.	β	111	0.1626	0.1606	F. C. C.
St.	α	111	0.1965	0.1952	„
M.	β	200	0.2175	0.2141	„
St.	α	200	0.2624	0.2603	„
W.	α	102	0.3630	0.3641	Hex.
W.	β	220	0.4298	0.4282	F. C. C.
W.	α	110	0.5029	0.5073	Hex.
St.	α	220	0.5224	0.5206	F. C. C.
W.	β	311	0.5885	0.5888	„
W.	α	103	0.6039	0.6079	Hex.
v. w.	β	222	0.6428	0.6424	F. C. C.
W.	α	112	0.6951	0.7023	Hex.
St.	α	311	0.7150	0.7146	F. C. C.

$\sin^2\theta$ is very good. From the above experiment it may be clearly seen that ϵ -phase only forms a hexagonal close packed lattice and it contains neither a face centred cubic lattice of Fe₄N nor a body centred cubic lattice of iron, that $\epsilon + \gamma'$ -phase is a mixture of a hexagonal close packed lattice of Fe₂N and a face centred cubic lattice of Fe₄N and does not contain a body centred cubic lattice of iron, and that similarly $\gamma' + \alpha$ -phase does not contain a hexagonal close packed lattice of ϵ -phase.

Table 4.
Powder photographs of iron nitride ($\alpha + \gamma'$) (5.52% N₂)
Fe-K-radiation.

Film dia. 60.1 mm.

Intensity.	Radiation	$h\ k\ l.$	$\text{Sin}^2\theta$ obs.	$\text{Sin}^2\theta$ calc.	Lattice
M.	β	111	0.1605	0.1606	F. C. C.
St.	α	111	0.1940	0.1952	„
W.	β	200	0.2151	0.2141	„
St.	α	200	0.2599	0.2603	„
W.	β	220	0.4281	0.4282	„
St.	α	220	0.5224	0.5206	„
W.	β	311	0.5894	0.5888	„
v. w.	β	222	0.6428	0.6424	„
St.	α	311	0.7142	0.7146	„

Table 5.
Powder photographs of iron. (α)
Fe-K-radiation.

Film dia. 60.40 mm.

Intensity	Radiation	$h\ k\ l.$	$\text{Sin}^2\theta$ obs.	$\text{Sin}^2\theta$ calc.	Lattice
W.	β	110	0.1876	0.1878	B. C. C.
St.	α	110	0.2272	0.2282	„
W.	β	200	0.3743	0.3756	„
M.	α	200	0.4547	0.4564	„
W.	β	211	0.5598	0.5633	„
St.	α	211	0.6800	0.6846	„
v. w.	β	110	0.7465	0.7511	„

III. Determination of the Heat of Formation of Fe₄N. When iron nitride is dissolved in dilute sulphuric acid, it is decomposed and yields salts of iron and of ammonium, hydrogen being evolved at the same time. This reaction offers a convenient method for the determination of the heat of formation of the nitride. The equation corresponding to the reaction is as follows :



The concentration of acid was 1.022 normal. Six hundred grams were introduced into a glass calorimeter, a very thin glass beaker of about 19 gr. in weight, provided with a cover and supported on three corks inside a Dewar's vessel. The liquid was agitated by a glass screw-stirrer revolving about four times a second, and a regular current of hydrogen was led through the calorimeter to prevent the oxidation of the ferrous sulphate formed. The calibrated Beckmann's thermometer was used. The apparatus is shown in Fig. 4.

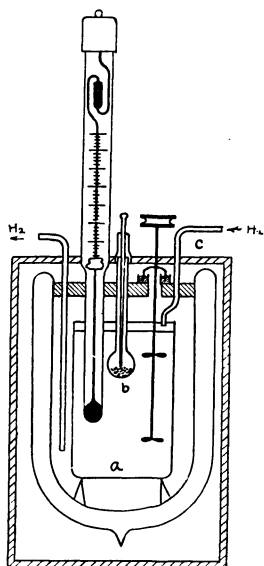


Fig. 4. Apparatus for measurement of heat of solution of iron nitride.

The thermometer was carefully observed until the rate of change was steady. Then the iron nitride, contained in *b*, was introduced into the calorimeter by breaking *b* by a glass rod and readings were taken every minute until the rate of change was steady. The reaction was a slow one; the time needed to accomplish each experiment was about 4 hrs. The correction was calculated graphically and the agreement of four results shows that the determinations are satisfactory. The solution yielded almost no coloration with potassium thiocyanate at the conclusion of the experiments.

The specific heat of the final solution was taken to be equal to that of the solution of sulphuric acid used. The specific heat was taken from the experiments of G. Agde and H. Holtmann⁽¹⁾, which gives 0.9598. The specimen used contains 6.53% nitrogen: mixture of 12.04% Fe_2N and 87.96% Fe_4N . The heat of solution of Fe_2N in dilute sulphuric acid was taken from the determination of G. Fowler, Ph. J. Hartog⁽²⁾ as 81.56 Cal. for 125.7 gr. of Fe_2N .

The details of the experiments are shown in Table 6.

Table 6. Details of the calorimetric experiments.

Number of experiment.	60	61	62	63	Mean
Composition of the nitride % N_2	6.53	6.53	6.53	6.53	
Water equivalent of calorimeter and contents. (including acid, stirrer, part of thermometer immersed etc.)	580.0	580.3	580.3	580.4	

(1) G. Agde und H. Holtmann, *Z. anorg. allgem. Chem.*, **158** (1926), 316.

(2) G. Fowler, Ph. J. Hartog, loc. cit.

Table 6.—(Continued.)

Number of experiment.	60	61	62	63	Mean
Weight of substance dissolved (gr.)	1.0005	1.0046	1.0032	1.0023	
Rise of temperature. (°C.)	0.930	0.954	0.927	0.937	
Cooling correction. (°C.)	0.031	0.034	0.028	0.023	
Total number of calories evolved. (Cal.)	0.5574	0.5734	0.5542	0.5572	
Calories evolved by the solution of Fe ₂ N. (Cal.)	0.0782	0.0785	0.0784	0.0783	
Calories evolved by the solution of 1 gr. Fe ₄ N. (Cal.)	0.5446	0.5600	0.5392	0.5432	0.5468
Thermal value of the reaction in calories.	129.74				

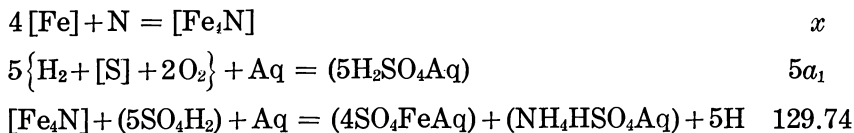
If we start from a given initial system and pass to a given final system by two different cycles of transformations, we may assume that the total heat evolved is in both cases the same.

We take as the initial system $4[\text{Fe}] + \text{N} + 10\text{H} + 5[\text{S}] + 20\text{O} + \text{Aq}$.

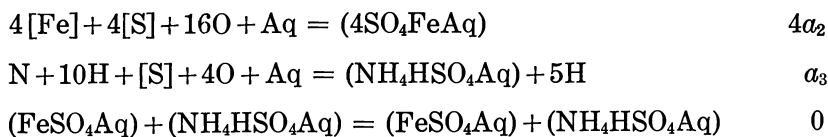
We take as the final system $(4\text{FeSO}_4\text{Aq}) + (\text{NH}_4\text{HSO}_4\text{Aq}) + 5\text{H}$.

Cycle I

Thermal value of reaction.



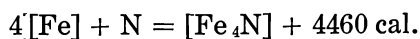
Cycle II



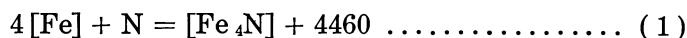
We have the equation $x + 5a_1 + 129.74 = 4a_2 + a_3$

According to Berthelot, $a_1 = 210.1$ Cal, $a_2 = 234.9$ Cal,

$a_3 = 245.1$ Cal, we find $x = 4.46$ Cal, i.e.,



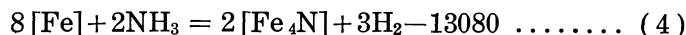
IV. Discussion of the Results. By combining the measured heat of formation of Fe_4N :



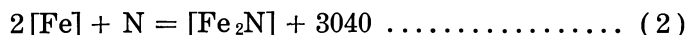
with the heat of formation of ammonia:



the author obtained the following result:



Similarly by combining the heat of formation of Fe_2N measured by G. Fowler, Ph. J. Hartog⁽¹⁾



with (1) and (3), he obtained the following result:



The author obtained the equilibrium equations of the reaction (4) and (5) by the use of the Nernst's heat theorem in order to compare them with the observed equilibrium data obtained by E. Lehrer⁽²⁾ at high temperatures. Lehrer's data are not obtained from pure Fe_2N , Fe_4N , Fe but from solid solutions ϵ , γ' , α . However, γ' and α may be regarded as almost same as pure Fe_4N and Fe respectively, therefore the author found it convenient to compare these data with his equation. ϵ can not be regarded as equal to pure Fe_2N but the author dared to compare his equation with these experimental data in the following way: Considering that the atomic heat of nitrogen is of course less than 6.4, he calculated the atomic heat of nitrogen from the observed molecular heats of some nitrogen compounds according to Neumann and Kopp's law assuming the atomic heat of oxygen to be 4, that of hydrogen to be 2.3 and those of other elements to be 6.4 each.

Nitrogen compounds. Calculated atomic heat of nitrogen.

NO_3Na	3.4
$(\text{NO}_3)_2\text{Ba}$	3.75
$(\text{NO}_3)_2\text{Sr}$	3.95
NH_4Cl	4.4
NO_3K	5.7
	4.24 (mean).

(1) G. Fowler, Ph. J. Hartog, loc. cit.

(2) E. Lehrer, loc. cit.

The mean atomic heat (4.24) thus obtained was used as the atomic heat of nitrogen in calculating the molecular heats of iron nitrides. From the above mentioned observed result, the heat of formation of Fe_4N (W_1) is expressed in the following equation :

$$4[\text{Fe}_4\text{N}] = 8[\text{Fe}] + \text{N}_2 - W_1 \quad 17^\circ\text{C.} \dots\dots\dots (6)$$

where, $W_1 = 8920$. On the assumption that W_1 varies with the temperature, W_1 may be expressed by a series containing only integral powers of T :

$$W_1 = W_{01} + 3.5 T + \alpha T^2 .$$

Differentiating with respect to T ,

$$\frac{dW_1}{dT} = \sum nC_p = 3.5 + 2\alpha T . \quad \text{where} \quad \sum n = 1 .$$

Assuming the atomic heat of iron to be 6.0, the molecular heat of gaseous nitrogen to be 6.9 and that of Fe_4N to be $6 \times 4 + 4.24 = 28.24$, we obtain

$$\alpha = \frac{6.9 + 8 \times 6 - 2 \times 28.24 - 3.5}{2 \times 290} = -0.008759 .$$

Therefore $W_1 = 8642 + 3.5 T - 0.008759 T^2$

The equilibrium equation of the reaction (6) can readily be obtained as shown below : The chemical constant of nitrogen is 2.6. Accordingly,

$$\sum m = 1 , \quad \sum mI = 2.6$$

Therefore,

$$\log P_{\text{N}_{2(g)}} = -\frac{8642}{4.571 T} + 1.75 \log T - \frac{0.008759 T}{4.571} + 2.6 \dots\dots\dots (7)$$

According to F. Haber⁽¹⁾, the variation of the equilibrium constant of ammonia is expressed by the following equation :

$$\log K_p = -\frac{4196}{T} + 5.0176 \log T + 0.0002012 T - 0.372 \times 10^{-6} T^2 - 4.2 \quad (8)$$

From (7) and (8), the equilibrium equation of the reaction (4) can readily be obtained as shown below :

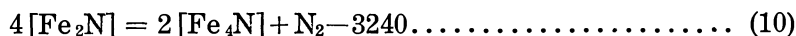
$$\log K_{p_1} = -\frac{2305}{T} + 3.2676 \log T + 0.0021174 T - 3.72 \times 10^{-7} T^2 - 6.8 \quad (9)$$

(1) F. Haber, *Z. Elektrochem.*, **20** (1914), 597.

According to G. Fowler, Ph. J. Hartog⁽¹⁾, the heat of formation of Fe_2N is expressed in the following equation :



From (1) and (2), we obtain



$$3240 = W_2$$

On the assumption that W_2 varies with the temperature, W_2 may be expressed similarly as in the case of W_1 as follows :

$$W_2 = W_{02} + 3.5 T + \alpha T^2 .$$

$$\text{Similarly, } \frac{dW_2}{dT} = \sum n C_p = 3.5 + 2 \alpha T, \quad \text{where } \sum n = 1 .$$

Assuming the molecular heat of Fe_4N to be 28.24, that of gaseous nitrogen to be 6.9 and that of Fe_2N to be $6 \times 2 + 4.24 = 16.24$, we obtain

$$\alpha = \frac{6.9 + 2 \times 28.24 - 4 \times 16.24 - 3.5}{2 \times 290} = -0.008759 .$$

$$\text{Therefore } W_2 = 2962 + 3.5 T - 0.008759 T^2$$

The equilibrium equation of the reaction (10) can similarly be obtained. As previously shown,

$$\sum m = 1, \quad \sum mI = 2.6 .$$

Therefore,

$$\log P_{\text{N}_2(2)} = -\frac{2962}{4.571 T} + 1.75 \log T - \frac{0.008759 T}{4.571} + 2.6 \dots\dots\dots (11)$$

From (11) and (8), the equilibrium equation of the reaction (5) can readily be obtained as before :

$$\log K_{p_2} = -\frac{3548}{T} + 3.2676 \cdot \log T + 0.0021174 T - 3.72 \times 10^{-7} T^2 - 6.8 \quad (12)$$

The agreement of the equilibrium constants at high temperatures between the calculated values according to the equations (9) and (12) and those observed by E. Lehrer⁽²⁾ is quite satisfactory as shown in Table 7 and Fig. 5.

(1) G. Fowler, Ph. J. Hartog, loc. cit.

(2) E. Lehrer, loc. cit.

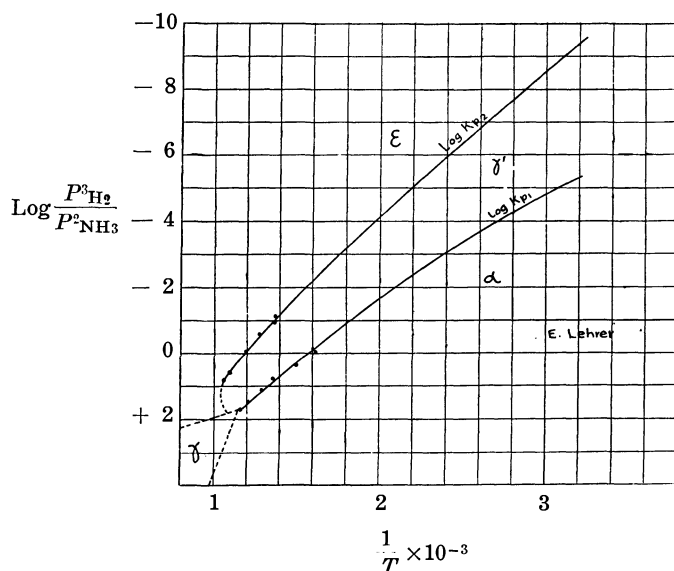
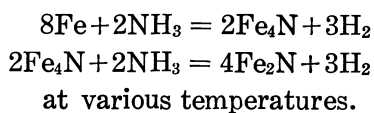


Fig. 5. Variation of equilibrium constants of
 $8\text{Fe} + 2\text{NH}_3 = 2\text{Fe}_4\text{N} + 3\text{H}_2$ ($\text{Log } K_{p1}$)
 $2\text{Fe}_4\text{N} + 2\text{NH}_3 = 4\text{Fe}_2\text{N} + 3\text{H}_2$ ($\text{Log } K_{p2}$)
 with temperature.

Table 7. Equilibrium constants of reactions:



$T^\circ\text{K}$	$8\text{Fe} + 2\text{NH}_3 = 2\text{Fe}_4\text{N} + 3\text{H}_2$ $\text{Log } \frac{P^3_{\text{H}_2}}{P^2_{\text{NH}_3}}$		$T^\circ\text{K}$	$2\text{Fe}_4\text{N} + 2\text{NH}_3 = 4\text{Fe}_2\text{N} + 3\text{H}_2$ $\text{Log } \frac{P^3_{\text{H}_2}}{P^2_{\text{NH}_3}}$	
	$\text{Log } K_{p1}$ (Author)	$\text{Log } K_{p1}$ (Lehrer)		$\text{Log } K_{p2}$ (Author)	$\text{Log } K_{p2}$ (Lehrer)
618	-0.243	-0.0637	729	-0.966	-1.123
623	-0.195	-0.1154	730	-0.957	-0.968
668	+0.228	+0.346	783	-0.444	-0.589
734	+0.779	+0.752	835	+0.007	-0.060
773	+1.070	+1.107	905	+0.553	+0.600
827	+1.445	+1.473	940	+0.802	+0.845
862	+1.669	+1.675			

The author deduced the following two empirical equations from the measured heat of formation at an ordinary temperature, in order to see whether these equations could express the observed data of E. Lehrer⁽¹⁾ or not :

$$\log K_{p'_1} = -\frac{13080}{4.571 T} + 4.775$$

$$\log K_{p'_2} = -\frac{18760}{4.571 T} + 4.775$$

At 734° K and 773° K, the observed equilibrium constants of the reaction (4) are +0.752 and +1.107 respectively while the corresponding calculated values are +0.876 and +1.073 respectively ($\log K_{p'_1}$). And at 730° K and 835° K, the observed data of the reaction (5) are -0.968 and -0.06 respectively while the corresponding calculated values are -0.847 and -0.140 ($\log K_{p'_2}$). In this case the agreement between the observed and calculated values is fairly good.

V. Electrochemical Properties of Iron Nitrides. As described in the previous paper⁽²⁾, single potential of nitrified iron in ferrous sulphate solution is greatly influenced by the presence of ferric ion. The author measured the single potential of ϵ , which was confirmed by X-ray to contain no iron.

ϵ -phase immersed in the ferrous sulphate solution (1 normal) free from ferric ion showed the potential of

$$\epsilon_h = -0.448 \text{ volt.}$$

which corresponds to the potential of powdered iron, but that immersed in the same solution containing 7 per cent. ferric ion showed the potential of

$$\epsilon_h = +0.5708 \text{ volt.}$$

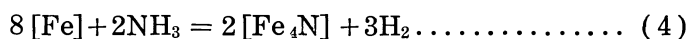
It is clear that the presence of ferric ion or oxygen changes the iron nitride into the passive state and that the single potential of iron nitride reported by F. Hanaman⁽³⁾ is nothing more than that of the passive iron nitride.

If the iron nitride does not show the passive state in the ammonia solution, cells may be constructed by suitable combination of nitrides and hydrogen electrode, and by measuring the electromotive force of these cells, equilibrium constants of the reactions :

(1) E. Lehrer, loc. cit.

(2) S. Satoh, *Am. Inst. Min. Met. Eng., Tech. Publ.*, No. 447 (1932).

(3) F. Hanaman, Dissertation Berlin, (1913).



could be directly measured.

ϵ -phase immersed in 1-normal ammonia solution shows the potential of

$$\epsilon_h = +0.199 \text{ volt,}$$

as shown in Fig. 6, but that immersed in the same solution free from oxygen shows the potential of

$$\epsilon_h = -0.713 \text{ volt.}$$

As may be seen, iron nitride shows no sign of changing into the passive state in the oxygen free ammonia solution.

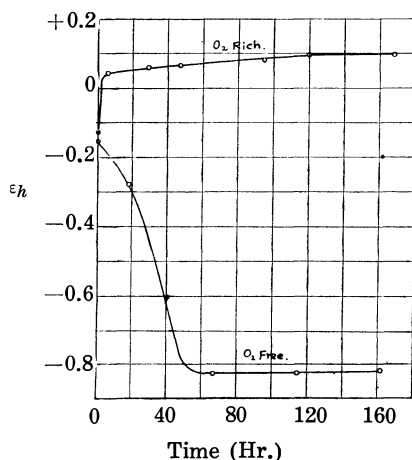
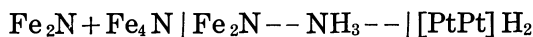
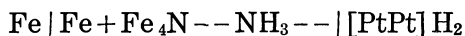


Fig. 6. Potential measurement of iron nitride 1-normal ammonia solution which contained oxygen or not.

If P_{H_2} denoted the partial pressure of hydrogen over ammonia solution and P_{NH_3} that of ammonia, and K_{p1} , K_{p2} the equilibrium constants of reactions (4) and (5) respectively, the electromotive force of the cells:



could be expressed in the following equations :

$$E_1 = \frac{RT}{nF} \left(\log K_{p_1} - \log \frac{P_{H_2}^3}{P_{NH_3}^2} \right)$$

$$E_2 = \frac{RT}{nF} \left(\log K_{p_2} - \log \frac{P_{H_2}^3}{P_{NH_3}^2} \right)$$

where $n = 6$ and $T = 308$. The values of $\log K_{p_1}$ and $\log K_{p_2}$ calculated from (9) and (12) are respectively -5.534 and -9.57 . The partial pressure of ammonia over 1-normal ammonia solution obtained from the curve based on the measurements of W. Gaus⁽¹⁾, R. Abegg and H. Riesenfeld⁽²⁾ is 22.1 mm. at 35°C. Therefore, the values of P_{NH_3} can be calculated by the formula of J. Lock and J. Forssall⁽³⁾ as follows :

$$P_{NH_3} = \frac{22.1 \times n + 0.18 n^2}{760} = 0.03095 \text{ at.},$$

where $n = 1.055$.

According to E. P. Perman⁽⁴⁾, the partial pressure of water over 1.055 normal ammonia solution can be calculated by the following formula :

$$p_0 = P \cdot (1-x) = 41.43 \text{ mm.},$$

in which p_0 are the partial pressures of water over the solutions, P are the pressures of pure water at the same temperature, and x is the fractional amount of ammonia in 1 gr. of the solution.

Therefore, the values of P_{H_2} can be calculated by the following formula :

$$P_{H_2} = \frac{760 - P - p_0}{760} = \frac{695.1}{760} = 0.9146 \text{ at.}$$

Therefore,

$$E_1 = \frac{0.0001983 \times 308}{6} (-5.534 - 2.90) = -0.0859 \text{ volt.}$$

$$E_2 = \frac{0.0001983 \times 308}{6} (-9.57 - 2.90) = -0.1269 \text{ volt.}$$

(1) W. Gaus, *Z. anorg. Chem.*, **25** (1900), 236.

(2) R. Abegg, H. Riesenfeld, *Z. physik. Chem.*, **40** (1902), 90.

(3) J. Lock and J. Forsall, *Am. Chem. J.*, **31** (1904), 268.

(4) E. P. Perman, *Trans. Chem. Soc.*, **79** (1901), 718; **83** (1903), 1168.

With the object of ascertaining these results, the author made experiments with the apparatus shown in Fig. 7. ϵ , $\epsilon + \gamma'$, $\gamma + \alpha$, and α , the compositions of which were determined by chemical analyses and X-ray, were used as specimens. α and $\epsilon + \gamma'$, compressed in cylindrical form, were soldered at their ends with copper wire. The soldered ends of the specimens α and $\epsilon + \gamma'$ were inserted into a glass tube *a* and *b* respectively, filled with solid paraffin to prevent the solution from entering into the soldered part. In *e* and *f* the powders of $\gamma' + \alpha$ and ϵ were introduced respectively. And *g* was filled with quartz sand purified with aqua regia. *h* is a hydrogen electrode and the purified hydrogen was passed through the tube *i*, and

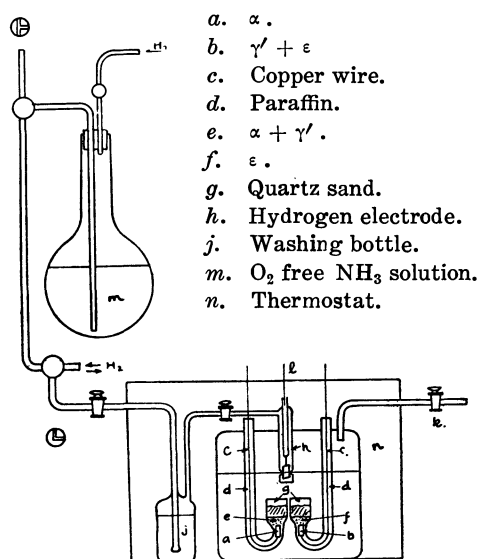


Fig. 7. Apparatus for measurement of the E. M. F. of the iron nitride cell.

through a solution of ammonia of the same concentration as was contained in the cell. *l*, *c* being connected with Leeds and Northrup potentiometer, the electromotive force of the cell was measured. The oxygen free ammonia solution was poured into the cell through *m*. The temperature of the cell was kept constant ($35^\circ \pm 0.2^\circ\text{C.}$) by means of the air thermostat. The results obtained are shown in Table 8, and the time voltage curves are shown in Figs. 8 and 9.

As may be seen from the curves, very constant voltage was obtained in each case and the final constant voltages were shown as below :

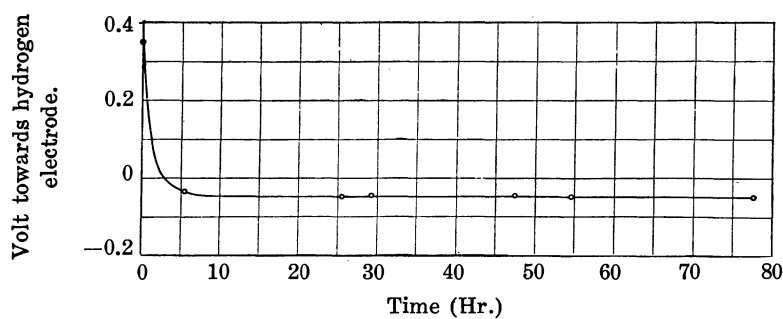


Fig. 8. Time voltage curve of iron nitride cell.

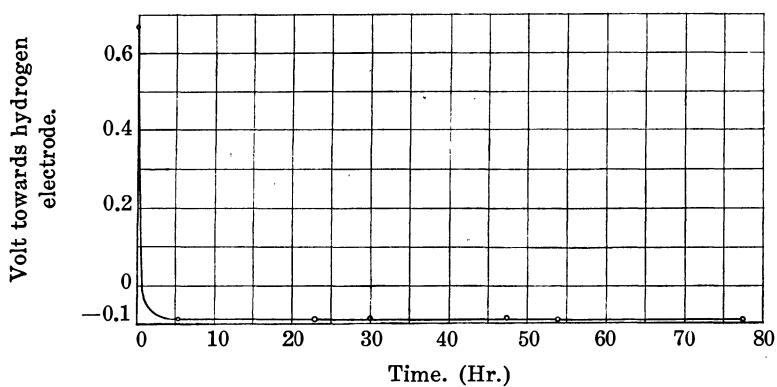
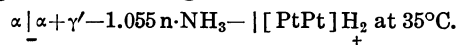


Fig. 9. Time voltage curve of iron nitride cell.

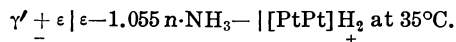


Table 8.

Potential measurement of iron nitride cells.

Temp. (°C.)	Time in NH ₃ solution. (Hr.)	$\alpha \alpha + \gamma' - 1.055 n \cdot \text{NH}_3 - [\text{PtPt}] \text{H}_2$	$\gamma' + \epsilon \epsilon - 1.055 n \cdot \text{NH}_3 - [\text{PtPt}] \text{H}_2$
		volt.	volt.
35	0	-0.3501	-0.6693
„	5.5	0.03232	0.08595
„	23	0.04965	0.08447
„	30	0.04564	0.08145
„	47.5	0.04507	0.07974
„	54.	0.04911	0.08309
„	77.5	0.04800	0.08270

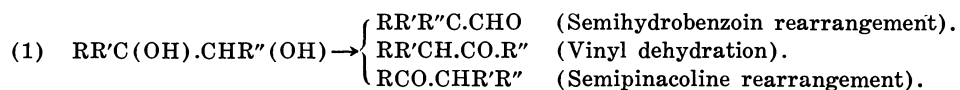
STUDIES ON MOLECULAR-REARRANGEMENTS OF α -GLYCOLS. IV. INFLUENCE OF SUBSTITUENTS ON A PINACONE IN ITS REACTIVITY. REDUCTION OF DI-*p*-METHOXY-BENZOPHENONE.

By Masao MIGITA.

Received September 17th, 1932. Published October 28th, 1932.

When trisubstituted α -glycols are treated with dehydrating agent, the influence of substituents can be seen chiefly in the mode of molecular rearrangement, and the reaction products are ketones or aldehydes.⁽¹⁾ $\alpha\alpha$ -Dimethyl- β -acetyl glycol, $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{COCH}_3$, is the only instance known in which a trisubstituted α -glycol undergoes simultaneously molecular rearrangement and dissociation into ketone and carbinol by the action of rearranging agents.⁽²⁾ The author has attributed the dissociation of this glycol to the presence of unstable linkage in the molecule between α and β carbon atoms. If it be so, aromatic pinacones are quite possible to give simultaneous reaction of rearrangement and dissociation under the same conditions, because they bear close resemblance to hexa-aryl ethanes with respect to the negativities of substituents and are assumed to have unstable linkages between the two adjacent carbon atoms in chain, owing to their strongly positive polarities. In fact, all known aromatic pinacones split into corresponding ketones and carbinols at their melting points, and particularly in the case of tetra-*p*-bromobenzopinacone, it is reported that pinacolone rearrangement and dissociation into ketone and carbinol take place simultaneously by the action of acetyl chloride.⁽³⁾ Under the same conditions, not a single case of dissociation has been reported with other aromatic pinacones with highly negative groups such as diphenyl, fluoryl or xanthyl.⁽⁴⁾

For the purpose of drawing some conclusion on the influence of negative substituents upon the reactivities of pinacones by collecting a series of new data, tetra-*p*-methoxybenzopinacone is first studied, because it contains anisyl radical which is regarded the most negative organic radical, and yet all that we can find in literature about it, is



(2) Migita, this Bulletin, **4** (1929), 225-234.

(3) Montagne, *Rec. trav. chim.*, **43** (1924), 126-142.

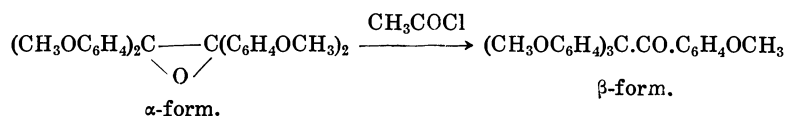
(4) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 236-257.

the following few lines with a proviso "unpublished" that anisyl pinacone, $(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{C}(\text{OH})\cdot\text{C}(\text{C}_6\text{H}_4\text{OCH}_3)_2(\text{OH})$, melts at 182°C . and re-melts at $117\text{--}118^\circ\text{C}$., if the melting point is remeasured after one hour with the same sample.⁽¹⁾

Reduction of Di-*p*-Methoxybenzophenone. In order to prepare the pinacone in question, the reduction of di-*p*-methoxy-benzophenone was tried by the following methods, which are usually employed for this purpose, namely, reductions by zinc dust and acetic acid, by absolute alcohol under direct sunlight, and by binary mixture of magnesium and its iodide in ether-benzene solution.

According to the authors⁽²⁾ the third method seems most suitable for preparation of pinacones with highly negative substituents, for it gives not only very satisfactory yields (75–100%) on many aromatic ketones, but also it enables us to reduce ketones such as dibiphenyl ketone, fluorenone, and xanthone, of which reduction to corresponding pinacones has been proved unsuccessful by other methods. However, in the case of dimethoxy-benzophenone, the reaction did not proceed smoothly and resulted in formation of a tarry matter, though the reaction was carried out under various conditions.

As the above method had proved unsuccessful, reduction by hot glacial acetic acid and zinc dust was tried. The reaction product, however, was not the expected pinacone, but the corresponding pinacolone, the rearrangement product of the pinacone. A similar case has been reported in reduction of *p*-methoxy-benzophenone.⁽³⁾ Supposing that this pinacolone formation was due to heating the reaction mixture, the reduction was repeated at room temperature by using the same reducing agents. But the product was not again the pinacone but the pinacolone. That this pinacolone is of β -form, and not of α -form with oxide-ring, was proved by its stability toward acetyl chloride, for the latter should be easily converted to the former by this treatment.



Lastly tetramethoxy-benzopinacone was obtained by reducing the ketone under direct sunlight with absolute alcohol in a sealed tube. This pinacone decomposes on melting, usually into dianisyl ketone and

(1) Bouvet, *Bull. soc. chim.*, [4], **15** (1915), 209.

(2) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 236–257.

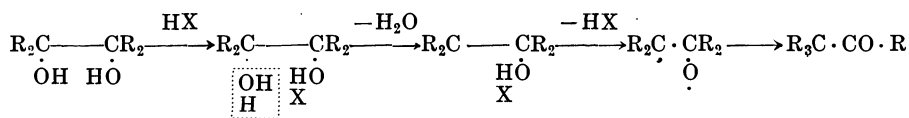
(3) Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37** (1925), 430.

dianisyl carbinol. Facility of rearrangement is one of the characteristics of this pinacone, and slightly warmed acetic acid is sufficient to convert it to the pinacoline. Though a close experiment was carried out in order to know if this pinacone undergoes dissociation as well as rearrangement by the action of acetyl chloride, no dissociation products were detected.

On the Facility of Rearrangement of Pinacones. (a) *Effect of Highly Negative Substituents.* The effect of negative substituents upon the reactivities of pinacones can be seen clearly in the reduction of benzophenone and its methoxy-derivatives by zinc dust and acetic acid (See the following table).

Reducing agent Ketone	Zinc dust and acetic acid	
	At room temperature	At higher temperature
$\text{CH}_3\text{OC}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{OCH}_3$	Pinacoline	Pinacoline
$\text{CH}_3\text{OC}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$	Pinacone ⁽²⁾	Pinacoline ⁽¹⁾
$\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$		Pinacone ⁽³⁾

In dimethoxy-benzophenone, pinacoline formation from ketone takes place even at room temperature, and in the case of methoxy-benzophenone at high temperature, while in benzophenone, pinacoline formation is not observed under these conditions. In order to convert benzopinacone into the pinacoline by the action of acetic acid, it is necessary to heat it in a sealed tube, at 180–200°C. Thus we can see a marked increase of reactivity of the pinacone caused by successive introductions of methoxy-radical into the benzophenone molecule; which will be easily explained from the mechanism of pinacoline rearrangement discussed in foregoing papers. According to the author's interpretation,⁽⁴⁾ the first stage of the pinacoline rearrangement is the attraction between one of the hydroxyl groups of the pinacone and the hydrogen ion of the acid, and the reaction proceeds in the following manner.



- (1) Tiffeneau and Orékhoff, *Bull. soc. chim.*, **37** (1925), 430.
 (2) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.
 (3) Zagumenni, *Ber.*, **14** (1881), 1402.
 (4) Migita, this Bulletin, **3** (1928), 312.

Evidently, the attraction between hydrogen ion and the hydroxyl group is stronger, according as the negativity of the latter is larger; then it follows naturally from the theory of induced alternate polarity that pinacones with highly negative substituents should undergo rearrangement with great facility. And in the case of tetramethoxy-benzopinacone, owing to the extreme negativity of anisyl radical, its hydroxyl groups may be supposed to have so strongly negative polarity as the rearrangement takes place even by the action of a weak organic acid at ordinary temperature.

(b) *Function of a Small Quantity of Iodine in Pinacoline Rearrangement.* Gomberg and Bachmann⁽¹⁾ reported that a crystal or two of iodine in hot acetic acid is sufficient to convert a number of aromatic pinacones, including benzopinacone, to the pinacolines. The function of iodine in this case is supposed either to increase the negativity of oxygen atom of hydroxyl groups by attracting its hydrogen atom, or to produce hydroiodic acid by reacting with acetic acid, which behaves as rearranging agent. Then, in the case of pinacones with extremely negative groups the rearrangement can occur by the action of acetic acid even in the absence of iodine, as seen in the case of tetramethoxy- and dimethoxy-benzopinacones. Besides these, sym. di-*p*-methoxy-di-*p*-ethoxy-benzopinacone, sym. di-*p*-methoxy-di-*p*-phenyl-benzopinacone and sym. di-*p*-anisyl-di- β -naphthyl glycol may be cited in illustration, which will be described in other papers.

Experimental Part.

***p*-Anisic Acid.** M. p. 182°C. Behrens⁽²⁾ describes that it crystallises in needles of straight extinction and of negative character, but the crystals must be chiefly of oblique extinction, since they belong to monoclinic system and the face most developed is (110).⁽³⁾ This was confirmed by actual observation.

Di-*p*-Methoxy-Benzophenone. This ketone was prepared from *p*-anisole and anisoyl chloride.⁽⁴⁾ It crystallises from alcohol in plates or needles with oblique extinction, melts at 143°C., and is difficultly soluble in ligroin and ether, and readily in acetone and chloroform. In concentrated sulphuric acid it dissolves with yellow colouration, which was reported to be red in literature.⁽⁴⁾

(1) Loc. cit.

(2) Behrens-Kley, "Organische Mikrochemische Analyse," p. 79.

(3) Groth, "Chemische Krystallographie" IV, p. 504.

(4) Schnackenberg and Scholl, *Ber.*, **36** (1903), 654.

Reduction of Di-p-Methoxybenzophenone.

Reduction by Zinc-Dust and Acetic Acid. (a) *At High Temperature.* To a boiling solution of 2.4 gr. of the ketone in 15 c.c. of acetic acid, 6.5 gr. of zinc dust were added in portions. The solution, assuming light greenish tint, was kept gently boiling for 3 hours. Excess of zinc dust was filtered hot from solution and washed thrice with hot glacial acetic acid. The filtrate and washings were poured into water. Slightly greenish precipitates were gathered and purified from alcohol. It forms slender needles with straight extinction and of negative character, melting at 140–141°C. with slight decomposition and solidified in a glassy mass. It is readily soluble in acetone and chloroform, sparingly in ether and hot ligroin, and moderately in alcohol. It dissolves in concentrated sulphuric acid with intense mixed colours of green, blue and violet which changed to purple on standing.

Analysis. Subst. = 0.1613; CO_2 = 0.4549; H_2O = 0.0884 gr.

Found: C = 76.9; H = 6.14%.

Calc. for $\text{C}_{30}\text{H}_{28}\text{O}_5$ (tetramethoxybenzopinacoline): C = 76.9; H = 5.98%.

Action of Acetyl Chloride. In order to determine whether this pinacoline is of α - or β -form, it was treated with acetyl chloride in benzene solution as in the manner described later. The purified product was proved to be unchanged pinacoline. Thereby it is shown that the pinacoline is of β -form.

Hydrolysis. After boiling 0.5 gr. of this pinacoline with alcoholic potash for 12 hours, the product was poured into water, and the filtered solution was acidified with hydrochloric acid. Separated acid was recrystallized from hot water and was easily identified as *p*-anisic acid.

(b) *At Room Temperature.* Two grams of the ketone were dissolved in sufficient glacial acetic acid to keep it in solution at room temperature and an excess of zinc dust was added to the solution. After allowing the mixture to stand at room temperature (20–30°C.) for four days, the solution, filtered from unchanged zinc dust, and poured into a large quantity of water. Yellowish precipitates were washed with cold ether and then recrystallised from alcohol. The product crystallises in colourless fine needles which melt at 141°C. and dissolve in concentrated sulphuric acid with mixed colours of intense green, blue and purple. It was identified as tetra-*p*-methoxy-benzopinacoline by mixed melting point test.

Reduction by Absolute Alcohol under Direct Sunlight. Four grams of dianisyl ketone and 20 c.c. of absolute alcohol were sealed in a tube and exposed in sunlight. In the first two days, the change of

the crystalline appearance in the tube was observed and the solution assumed yellowish tint. After a week, the tube was opened and granular crystals were filtered off from the solution smelling richly of acetaldehyde. The crystals were treated with hot 95% alcohol repeatedly to remove unchanged dianisyl ketone, until the residue, obtained by evaporation of the alcoholic solution, gives with concentrated sulphuric acid intense blue coloration, free from yellow tint produced when the ketone is present. This procedure accompanies considerable loss of pinacone, but we can obtain the pinacone with reliable melting point only in this way. The product crystallises from a quantity of alcohol in white microscopic prisms with straight extinction and of positive character. It decomposes at melting point which is 176°C . when the temperature of the bath is slowly raised, and 181°C . when heated quickly. It re-melts, after solidification, at $123\text{--}125^{\circ}\text{C}$., while $117\text{--}118^{\circ}\text{C}$. is given by Bouvet.⁽¹⁾ It dissolves in concentrated sulphuric acid imparting to the solution mixed colours of intense blue and violet.

Anal.: Subst. = 0.1118; CO_2 = 0.3028; H_2O = 0.0636 gr.

Found: C = 73.8; H = 6.34%.

Calc. for $\text{C}_{30}\text{H}_{30}\text{O}_6$ (tetramethoxybenzopinacone): C = 73.9; H = 6.18%.

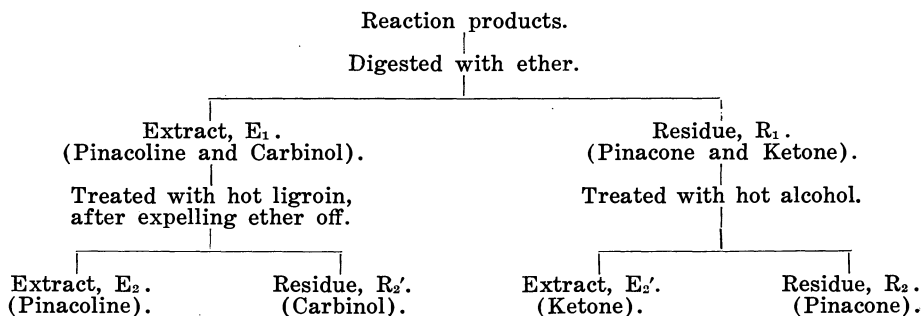
Reduction by Gomberg's Binary Mixture. To a boiling suspension of 1 gr. of magnesium in the solvent consisting of 15 c.c. of absolute ether and 20 c.c. of benzene, 1 gr. of iodine was added and the content was kept briskly boiling until practically colourless solution was obtained (about for one hour). The solution of magnesium iodide was cooled, to which 1 gr. of di-*p*-methoxy-benzophenone dissolved in 10 c.c. of warm benzene was added, and the content was shaken. During this process, heat was evolved and the solution became opaque and assumed brownish-red colour. The solution was gradually clarified and coloured deep red, while magnesium was coated with sticky substance, presumably owing to the formation of complex between the ketone and magnesium iodide. The content was shaken with repeated additions of fresh magnesium but every time it was coated immediately. When the reaction mixture was shaken for ten hours with a great excess of magnesium (a hundred times of theoretical amount), or heated to boiling to complete the reaction with efficient condenser of which upper end was stoppered, the solution was coloured dark and magnesium was uncoated. On hydrolysis, brown resinous matter was obtained which gave yellowish-brown amorphous substance (about 0.1 gr.) when purified from alcohol. The product, however, was not the pinacone nor the pinacoline in question, since it dissolves in concentrated sulphuric acid with reddish-brown colouration.

Some Reactions of Tetramethoxybenzopinacone.

Analytical Procedure. Separation of the pinacone, and its rearrangement and decomposition products in the presence of one another,

(1) Loc. cit.

which is indispensable in the study of reactions of tetramethoxybenzopinacone, was effected by the following scheme:



Of course, complete separation is attained by no means in this way, but it is not difficult to obtain a pure compound by further recrystallisation. For their identification, besides melting point and mixed melting point test, the colour reaction with concentrated sulphuric acid proved of good service.

Decomposition at Melting Point. 0.2 Gr. of the pinacone was heated at 185°C. for one hour, the cooled mass was powdered and analysed after the above process. The same white crystalline substance was obtained both from R_1 and E_2 which was identified as dimethoxybenzophenone. Repeated recrystallization of R'_2 , a semi-solid, from chloroform and ligroin, did not succeed in isolation of a compound with definite melting point. But it can be assumed to be dimethoxybenzohydrol by its behaviour toward solvents and by red colouration produced when dissolved in concentrated sulphuric acid.

Rearrangement of the Pinacone. (a) *Action of Hot Glacial Acetic Acid.* 0.1 Gr. of the sample was heated with 2 c.c. of glacial acetic acid at 100°C. for ten minutes, the content was poured into water and analysed. Tetramethoxybenzopinacolone, which melts at 140°C. with slight decomposition and solidifies in a glassy mass was obtained.

(b) *Action of Acetyl Chloride.* Two grams of the pinacone was dissolved in a mixture of 50 c.c. of dry benzene, 20 c.c. of acetyl chloride and 10 c.c. of glacial acetic acid, and was gently boiled for eight hours. After distilling the benzene off, the content was treated in the same way as in the last case. Tetramethoxybenzopinacolone was the only product isolated, dianisyl ketone and dianisyl carbinol being not detected.

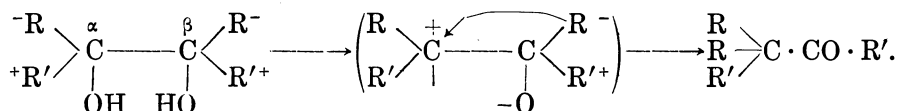
Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

STUDIES ON MOLECULAR-REARRANGEMENTS OF α -GLYCOLS. V. RELATIVE ELECTRONEGA- TIVITIES OF *p*-METHOXY-PHENYL AND *p*-ETHOXY-PHENYL RADICALS.

By Masao MIGITA.

Received September 17th, 1932. Published October 28th, 1932.

The author has observed that tetra-*p*-methoxybenzopinacone shows extreme facility to undergo molecular rearrangement and has attributed this behaviour to accumulation of strongly negative substituents in the molecule.⁽¹⁾ In order to confirm this assumption by another example on the one hand, and to compare relative electronegativities of *p*-methoxyphenyl and *p*-ethoxyphenyl radicals on the other hand, the reduction of 4-methoxy-4'-ethoxy-benzophenone and the rearrangement of the corresponding pinacone are studied. The principle of the determination of relative electronegativities of organic radicals by pinacolone rearrangement is based on the fact that in the rearrangement of *symmetrical* pinacone, $RR'C(OH) \cdot C(OH)RR'$, migration of the more negative radical, say R, takes place principally, and pinacolone $RRR' \cdot C \cdot CO \cdot R'$ is the chief product.⁽²⁾ This selective migration of the substituents in the rearrangement of a symmetrical pinacone can be interpreted as follows:



The α carbon atom in the fraction of molecule, $RR'C \cdot CO \cdot RR'$, which is assumed to be produced intermediately, is highly negatively polarized, since this carbon atom has been deprived of a part of its bond-forming electrons with the elimination of hydroxyl group. Therefore, if a radical migrates to this carbon atom from the other, the more negative radical is naturally assumed to wander with greater easiness.

As for the relative electronegativities of lower alkyl radicals, the results given by different methods are not concordant, but it is generally accepted that no parallelism exists between electronegativities of alkyl

(1) Migita, this Bulletin, **7** (1932), 336.

(2) We can find a series of such cases in literature, for example, $R = C_6H_5$, $R' = CH_3$; $R = CH_3OC_6H_4$, $R' = C_6H_5$; $R = C_6H_5C_6H_4$, $R' = C_6H_5$.

radicals and the number of their carbon atoms and that methyl radical is more electronegative than ethyl.⁽¹⁾

Now, if methyl radical is more negative than ethyl, in the case of alkoxy-radicals the relation of negativities will be inversed by the theory of induced polarity, ethoxy being more negative than methoxy radical. Nextly when this methoxy or ethoxy radical enters in phenyl radical at para position, the relation of electronegativities between these alkoxy-phenyl radicals are the same with that between the original alkoxy radicals, since the effect of the negativities of alkoxy radicals appear alternately in the carbon atoms of the benzene ring. Thus *p*-ethoxy-phenyl will be more negative than *p*-methoxy radical.

Now, in the actual rearrangement of sym. dimethoxy-diethoxy-benzopinacone, migration of ethoxy radical took place almost exclusively and 4-methoxyphenyl-bis(4'-ethoxyphenyl)-4''-methoxybenzoyl-methane, $(C_2H_5OC_6H_4)_2(CH_3OC_6H_4)C.CO.C_6H_4OCH_3$ was produced. This shows, as expected, that *p*-ethoxyphenyl radical is more negative than *p*-methoxyphenyl, and thereby, it gives an indirect proof on the more negative character of methyl radical than ethyl.

On reduction by glacial acetic acid and zinc dust, 4-methoxy-4'-ethoxybenzophenone gives corresponding pinacoline, as in the case of dimethoxybenzophenone. This is to be expected, as both the ketones are accumulated with highly negative radicals.

It is highly interesting that a fair quantity of the pinacoline, but no pinacone, was isolated from reduction products of this ketone by absolute alcohol under direct sunlight, while in the case of dimethoxybenzophenone, pinacone was the only product. It is inferable, thereby, that between these two substituted benzophenones the former exceeds the latter in its reactivity, which is consistent with the fact that *p*-ethoxyphenyl is more negative than *p*-methoxyphenyl radical, since the reactivity of a pinacone is considered to increase according as the negativities of substituents are raised.⁽²⁾ As for the mechanism of pinacoline formation by this reduction, it was assumed if a minute quantity of

-
- (1) $C_3H_7 > CH_3 > C_2H_5$, by carbinol method (Skraup, *Ber.*, **55** (1922), 1074).
 $CH_3 > C_3H_7 > C_2H_5$, by pinacoline method (Meerwein, *Ann.* **419** (1919), 121.)
 $CH_3 > C_2H_5 > C_3H_7$, by dialkylmercury method (Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130).

Skraup and Meerwein did not use the term "electronegativity," but employed the term "affinity requirement." These two expressions, however, are the same in essence, since "affinity requirement" can be understood from electronic conception of valency as affinity for binding electrons.

- (2) Migita, this Bulletin, **7** (1932), 336.

acetic acid was produced by oxidation of alcohol, and if this alcoholic acetic acid behaved as rearranging agent. This assumption, however, was given up for the actual reduction products did not give acidic reaction.

Experimental Part.

4-Methoxy-4'-Ethoxy-Benzophenone, $\text{CH}_3\text{OC}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$. *p*-Anisoyl chloride, prepared from 15 gr. of *p*-anisic acid and a slight excess of thionyl chloride, was reacted in the presence of 12 gr. of aluminium chloride with 13 gr. of phenetol in carbon bisulphide solution. The reaction proceeded very smoothly and completed in few hours. On hydrolysing the aluminium complex, dark brownish heavy oil was obtained, which solidified in buttery mass by repeated steam distillation alternately in very weak acid and alkaline reactions. From hot alcoholic extract of this buttery mass 4-methoxy-4'-ethoxy-benzophenone crystallised out in scales with pearly lustre, which were drained on porous plate. Recrystallised methoxy-ethoxy-benzophenone melts at 106–107°C., is readily soluble in hot ligroin and cold ether, and difficultly in cold alcohol and acetic acid. When recrystallised from ligroin, the ketone precipitates in gelatinous mass. It dissolves in concentrated sulphuric acid with yellow colour.

Anal.: Subst. = 0.0742; CO_2 = 0.2030; H_2O = 0.0415 gr.

Found: C = 74.7; H = 6.22%. Calc. for $\text{C}_{16}\text{H}_{16}\text{O}_3$ (Ketone): C = 75.0; H = 6.26%.

4-Methoxyphenyl-bis (4'-Ethoxyphenyl)-4''-Methoxybenzoyl-Methane, $(\text{CH}_3\text{OC}_6\text{H}_4)(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4)_2\text{C}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{OCH}_3$. (a) *Reduction by Hot Acetic Acid and Zinc Dust*. Three grams of zinc dust were added in portions to gently boiling solution of 1.35 gr. methoxyethoxybenzophenone in 6 c.c. acetic acid. After four hours' boiling, acetic acid solution, filtered from unchanged zinc dust, was poured into a large quantity of water, pale yellowish flocculent precipitates being obtained. The unchanged zinc dust was treated twice with hot acetic acid and the combined extracts were treated in the same way. The crude product was readily soluble in ether, but in the solution it became free from yellow impurities and the ketone separated out as colourless granular crystals. Purifications from other solvents could not bring desired results. It melts at 160°C. and solidifies vitreously. It is readily soluble in benzene, and moderately in hot ligroin but sparingly in cold. It dissolves in concentrated sulphuric acid with dark brown colour which changes to

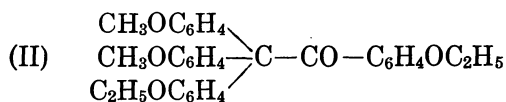
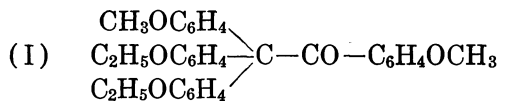
intense bluish purple. The product was found, by analysis, to be the corresponding pinacolone, but not the pinacone.

Anal.: Subst. = 0.0696; CO_2 = 0.1970; H_2O = 0.0415 gr.

Found: C = 77.2; H = 6.61%.

Calc. for $\text{C}_{32}\text{H}_{32}\text{O}_5$ (Pinacolone): C = 77.5; H = 6.45%.

Constitution. By reduction of methoxyethoxybenzophenone, we may have two isomeric pinacolines, I and II, which will give on hydrolysis with alcoholic potash *p*-anisic acid and *p*-ethoxybenzoic acid respectively.



In order to determine which of these two possible pinacolines has been actually obtained, the reduction product was hydrolysed by boiling with 20% alcoholic potash for twelve hours. After distilling off alcohol under diminished pressure, water was added to dissolve the potassium salt of organic acid. The neutral product which present as precipitates was extracted with benzene. The aqueous solution was acidified with sulphuric acid and was extracted with benzene. After removal of the solvent, the acid was treated with boiling water, in which *p*-anisic acid should be readily soluble while *p*-ethoxybenzoic acid only in trace. Actually the product was found dissolved in hot water completely. By repeated recrystallisations from hot water, fine colourless needles melting at 184°C . were obtained, which were identified as *p*-anisic acid by mixed melting point test, and by optical properties of the crystals. Thus the pinacolone was proved to be 4-methoxyphenyl-bis(4'-ethoxyphenyl)-4''-methoxybenzoyl-methane, corresponding to formula I.

(b) *Reduction by Absolute Alcohol under Direct Sunlight.* Methoxyethoxybenzophenone, dissolved in hot absolute alcohol, was sealed in a tube and exposed under direct sunlight. White crystals which fulfilled the tube disappeared in the course of several days and lightly yellowish-brown solution was obtained. The formation of acetaldehyde was easily detected by its peculiar smell and the sharp colour reaction toward Schiff's reagent. On distilling alcohol off under reduced pressure, greenish-gray soft mass was obtained, which was easily soluble in ordinary solvents except petroleum ether and ligroin. The crude product

was dissolved in small amount of alcohol and the solution was kept below 0°C. In the course of few days crystals appeared, from which the mother liquor was decanted off. But as the crystals were still contaminated with sticky impurities, dissolution and cooling were repeated twice, and finally they were purified from ether. The product crystallises in granules, melting at 160°C., and dissolves in concentrated sulphuric acid with colouration of dark brown which changes to intense bluish-purple. No depression of melting point was observed when mixed with the pinacoline obtained by reducing the original ketone by zinc dust and glacial acetic acid. From the fraction readily soluble in alcohol no definite compound could be isolated.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

ON THE COPPER AGE IN ANCIENT CHINA I.

By Tsurumatsu DŌNO.

Received September 21st, 1932. Published November 28th, 1932.

It has been generally believed that, in ancient civilized lands, the material civilization began at the age, in which stone implements were made use of, then entered into the metallic age and has come up to our days, passing through the ages of copper, bronze and iron implements, time after time. Now, it has also been stated by the relics unearthed from old sites that in ancient China there existed the stone age. As to the beginning of the bronze age in China, it is now supposed to date back to remote antiquity, though its absolutely exact period of appearance has been yet unknown. This fact is certified by a good deal of remains of those days which now exist, and it has been properly recognized that, in Chou dynasty (周代), various kinds of very exquisite bronze implements had already been manufactured. Further, in Chou-Li K'ao-Kung-Chi (周禮考工記) which is considered to be written in former Han (前漢) or before that dynasty—namely Ch'in dynasty (秦代) or Chan-Kuo period (戰國時代)—the following sentence can be found:—

金有六齊。六分其金而錫居一謂之鐘鼎之齊。五分其金而錫居一謂之斧斤之齊。四分其金而錫居一謂之戈戟之齊。三分其金而錫居一謂之大刃之齊。三分其金而錫居二謂之削殺矢之齊。金錫半謂之鑒燧之齊。

The Chinese classics above cited, displays the following meaning—that is, for bronze there are six mixtures according to their uses.

6	Parts of copper	and 1	part of tin,	is used for	bells and vessels etc.
5	"	"	1	"	socketed axe-heads.
4	"	"	1	"	halberds.
3	"	"	1	"	swords.
5	"	"	2 parts	"	arrow-heads.
1	Part	"	1 part	"	plane or concave mirrors. ⁽¹⁾

This sentence makes us to infer that, in those days, according to the purposes in which bronze was employed, the proportions between

(1) Metallic tools which were used for taking fire focussing the sun-light.

Chin⁽¹⁾ (金) and tin in bronze were astonishingly well studied, and it may be said that the proportions of those two metals and the way by which those alloys were employed, mentioned in above sentence, are almost quite right from the standpoint of the alloyage of the recent time, although there exist a few points to be corrected. In another chapter of Chou-Li K'ao-Kung-Chi (周禮考工記), the following sentence can be found:—

凡鑄金之狀。金與錫黑濁之氣竭黃白次之。黃白之氣竭青白次之。

青白之氣竭青氣次之。然後可鑄也。

This shows us the casting process of bronze in those days. In these words, we can find that even in those ancient times, the coloured flame reaction was properly utilised to decide the best chance for casting (casting temperature): namely, ancient Chinese founders performed the casting at the time in which copper was molten entirely and evolved the blue flame of copper.

Conclusively, we can say that at the time in which Chou-Li K'ao-Kung-Chi (周禮考工記) was written, they had already possessed quite advanced knowledge about bronze. Besides this, it has been considered that iron weapons in China were appeared at first time at the end of Ch'un-Ch'iu dynasty (春秋時代) or at the beginning of Chan-Kao period (戰國時代), and gradually increasing the use of them. And the age in which the most parts of weapons were made of iron, was considered to be about at the end of former Han dynasty (前漢代); therefore we can conclude that during the intervals of Ch'un-Ch'iu dynasty (春秋時代), Chan-Kao period (戰國時代), Ch'in dynasty (秦代) and the upper age of former Han dynasty (前漢代) there was bronze-iron age, and after the end of former Han dynasty (前漢代) the pure iron age in China first took its appearance. In archaeology, as a rule, the ages of stone, copper, bronze and iron being classified according to the materials used for weapons, of course it must be said that bronze was not given up to use for every tools except weapons even after the end of former Han dynasty (前漢代).

As was described above, the existence of the stone and the bronze age in ancient China has been admitted with certainty. But the exis-

- (1) Chin (金)—Here Chin means not gold but copper, in ancient China the whole metals were denoted by this letter Chin, and it was classified by colour into three species so-called San-P'in (三品)—that is, Huang-Chin (黃金), Po-Chin (白金) and Ch'ih-Chin (赤金)—and a little after, into five classes called Wu-Chin (五金)—namely Huang-Chin (黃金), Po-Chin (白金), Ch'ih-Chin (赤金), Ch'ing-Chin (青金) and Hei-Chin (黑金) or Hsüan-Chin (玄金). But, in general with a few exceptions, it also means copper alone. Perhaps copper was the most universal and representative kind of metals at that times; therefore copper was denoted by this letter Chin (金).

tence of the copper age in China has been considered in question, and even if it has really existed, its annalistic age would be beyond our imagination, on account of the want of copper implements which have never been discovered up to the present time (the word of copper does not mean chemically pure copper, but it means copper which is not artificially mixed with tin. Therefore it is allowable for the existence of other metals than tin, as impurities or from other standpoints).

As is well known, however, many remains of copper implements were discovered in ancient Egypt and other civilized lands, and it is said that in Egypt copper implements were used during long times, but this metal having been found too soft, several methods of copper-hardening were devised by Egyptian and after long and elaborated studies, bronze was at last brought into the world. In ancient China, therefore, the appearance of the bronze age after the stone age, skipping over the copper age, as is generally considered, seems somewhat improper, regarded from the orders of transition of utilization of metals. Taking these points in consideration, author has always suspected that the copper age must also have existed in China like in Egypt, although it has not been confirmed.

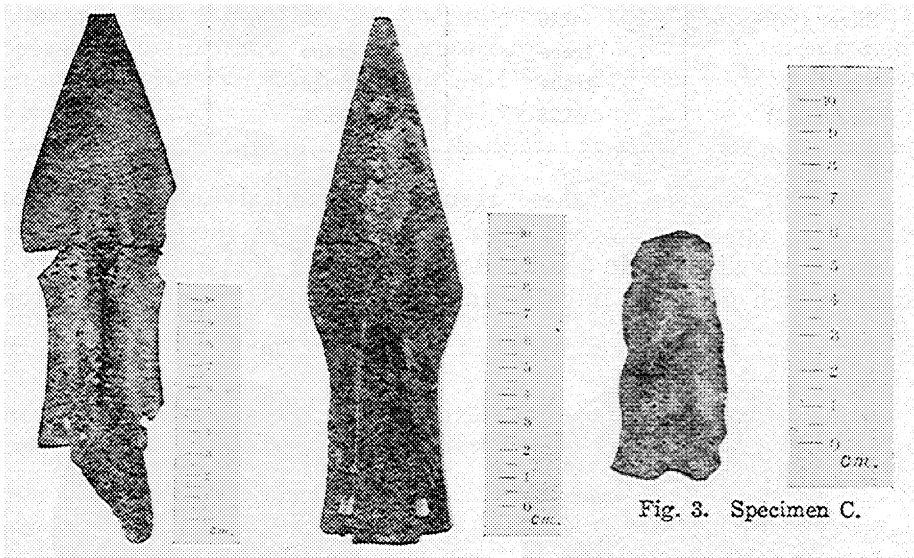


Fig. 1. Specimen A.

Fig. 2. Specimen B.

Fig. 3. Specimen C.

Quite recently author could have an occasion to carry out chemical studies of several crude spear-heads (Figs. 1, 2 and 3), for the kind deliverance of which he is very much indebted to the Archaeological

Institute of the Faculty of Literature of the Tokyo Imperial University. These spear-heads closely resemble with the relics recently unearthed from Yin site in Ho-Nan Province (河南省殷墟) in China. The results of the chemical analyses showed that these ancient Chinese spear-heads contain no significant amount of tin (indeed we could detect the metal only by arc spectral analysis, but as very faint lines). Now, author can conclude that these spear-heads must rather be called copper implements than bronze ones and thus he could here confirm that, in ancient China, there existed also the copper age like in ancient Egypt and other civilized lands. This will be in no less interest on the cultural history of China.

The results of the chemical analyses are as follows:—

	Specimen A	Specimen B	Specimen C
Sample (gr.)	0.4770	0.4266	0.5020
Copper (%)	91.36	72.68	57.17
Lead (%)	2.90	22.38	26.78
Iron (%)	1.42	2.12	1.05
Arsenic (%)	trace	0.80	trace
Silver (%)	0.10	0.30	0.05
Gold (%)	trace	trace	trace
Tin (%)	trace	trace	trace
Totals (%)	95.78	98.26	85.05

As will be seen in these results of chemical analyses, the total values are considerably less than 100%; among these, the specimen C is only about 85% in total. Author believes that this is due to the oxides which goes far into the inner part of the material and, there-

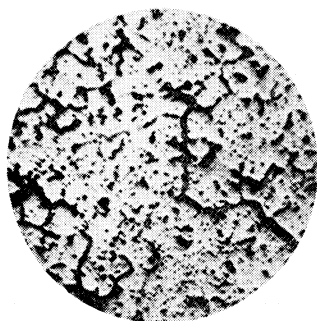


Fig. 4. Specimen A (Surface).

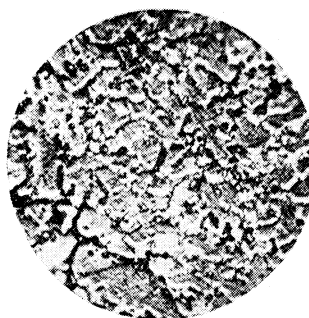


Fig. 5. Specimen A (Etched surface).

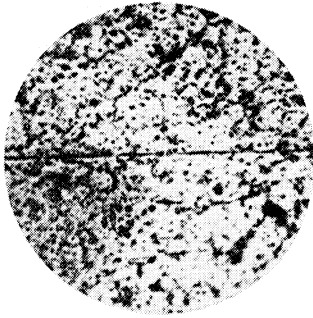


Fig. 6. Specimen A (Cross section).

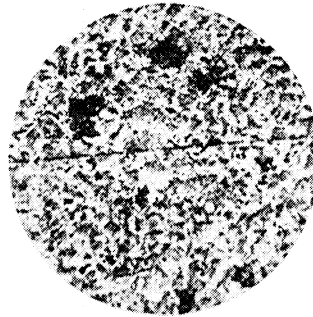


Fig. 7. Specimen A (Etched cross section).

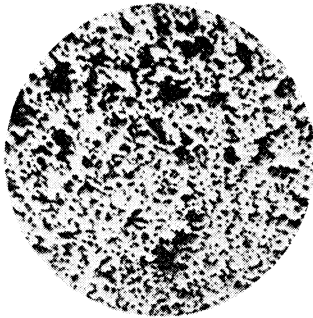


Fig. 8. Specimen B (Surface).

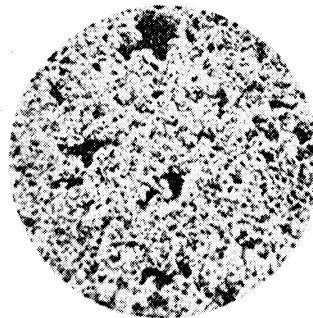


Fig. 9. Specimen B (Etched surface).

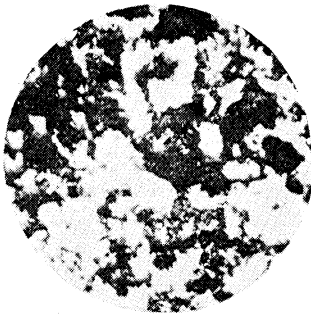


Fig. 10. Specimen C (Surface).

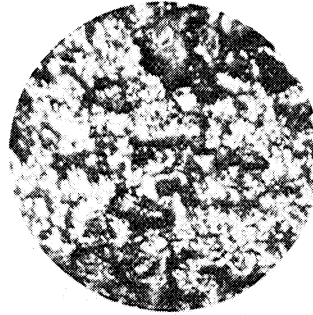


Fig. 11. Specimen C (Etched surface).

fore, a considerable amount of oxygen should be added to the elements above analysed. This can also be confirmed by the metallographical photograms (enlarged 100 times and etched by the solution of ammoniacal hydrogen-peroxide). It may be considered that the oxides in these specimens were produced by the following two causes: (1) as the technique of casting was still in its infancy in those days, oxidation

was not properly prevented at the time of melting, and (2) the materials have passed so long time as many thousand years, so that oxidation took place unartificially.

As for lead which is contained often in considerable quantities in the samples, it is hardly possible to think that it came from copper ores and it must rather be considered that this metallic element was artificially added in order to increase the fluidity of molten copper and to make the casting more easy. It will be no doubt that the other metals than copper and lead detected in the samples are contained as impurities which were impossible to be eliminated by the primitive metallurgical technique of those ancient days.

In conclusion, the author expresses his sincere gratitude to Prof. Dr. Y. Shibata, Prof. Dr. S. Katō and Prof. Dr. K. Kimura for their kind guidances, and to Prof. Dr. Y. Harada, Dr. K. Komai and Dr. N. Egami in the Archaeological Institute of the Faculty of Literature of Tokyo Imperial University, who offered the invaluable specimens for his chemical research, and also to Prof. Dr. T. Mishima for the trouble of taking the metallographical photographs.

Summary.

(1) Three specimens of ancient Chinese spear-heads which are said unearthed from Yin site (殷墟) were analysed, and it was found that they consist mainly of copper added with certain quantities of lead and contain no significant amount of tin.

(2) From the chemical studies, all these spear-heads are by no means of bronze and they are regarded as the first pure copper implements ever discovered in China.

(3) The prevailing opinion which negates the existence of the pure copper age in ancient China must thus be abandoned, and the existence of the copper age in China must be admitted.

(4) It is supposed that if these specimens were actually manufactured in Yin dynasty (殷代), the pure copper age in China existed at about Yin dynasty (殷代), and the beginning of the bronze age followed that age.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

A SPECTROCHEMICAL STUDY ON THE CHEMICAL CONSTITUTION OF A REACTION PRODUCT BETWEEN CENTRALITE AND GASEOUS NITROGEN PEROXIDE. DINITRODIPHENYLETHYLUREA.

By Kôiti MASAKI.

Received September 28th, 1932. Published November 28th, 1932.

Diphenyl-diethyl-urea, known as "CENTRALITE" (C/L), is used in several countries as a good gelatinizer or stabiliser for the smokeless powders and is now investigated in many explosives laboratories in the world. The great stabilizing effect of this substance is no doubt due to reaction of it with formation of stable nitrocompounds, preventing the injurious action of NO_2 gas and its acids produced by the spontaneous decomposition of nitroglycerine and nitrocellulose. From the stability point of view, it is an interesting and important problem, to see whether tetranitrocentralite is formed or not by the reaction between centralite and NO_2 gas at room temperature. In the Note,⁽¹⁾ published in 1926, M. A. Apard reported on the formation of tetranitrocentralite which was obtained in a very small quantity as deep yellow powder by crystallizing the residue, produced with extraction by benzene solution, with ethyl alcohol. It is, however, doubtful whether the yellow powder is really tetranitrocentralite or not, because of the very small quantity. The author carried out the reaction between NO_2 gas and powdered centralite almost in the same manner, the time of the reaction being a little longer, and was able to separate a small quantity of yellow powder from a dark reddish, syrupy mass of the reaction product by treating with benzene. This powder crystallized from acetone as minute thin plates, melting at $207\text{--}210^\circ\text{C}$., somewhat different from the melting point (175°C .) of tetranitrocentralite.

The author started to study the absorption spectra of centralite, dinitrocentralite, tetranitrocentralite and the sample in question. The following figure shows a comparison of the absorption curves. Optical behaviours of the unknown compound resemble to that of dinitrocentralite, the absorption maximum of which is observed at $3200\text{\AA}$, while that of the former at $3350\text{\AA}$. On the other hand, the tetranitrocentralite is found to show no selective absorption. The small difference between absorption spectra of the unknown substance and dinitro-

(1) *Mém. Poudres*, **22** (1926), 181.

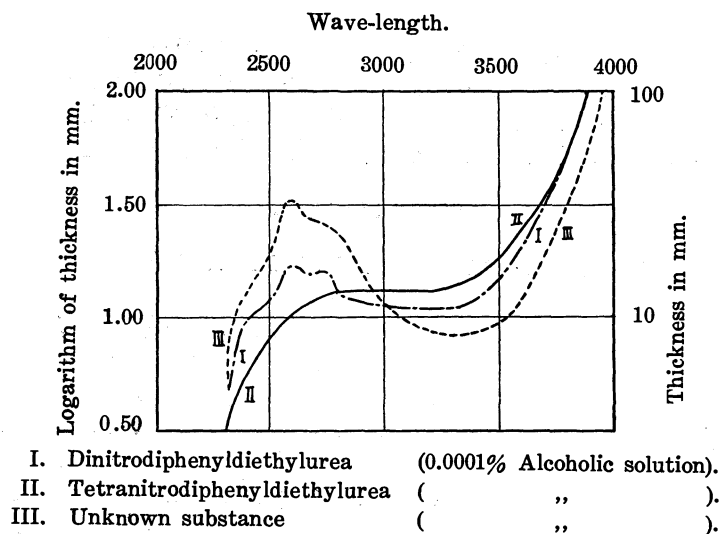


Fig. 1.

centralite has been investigated position and number of nitrogroups.

Nitrogen content in the unknown substance determined by micro-analysis (micro-duma.) is given below.

Subst. = 2.20 mg.; N_2 = 0.319 c.c. at 26.0°C and 759 mm. Found: N = 16.6 %.

The relation between number of nitrogroups and nitrogen percentages in nitro-compounds of centralite is shown in the following table.

	mono.	di.	tri.	tetra.
N%	13.59	15.63	17.81	18.75

Thus the new substance can hardly be expected to be other than dinitro- or trinitro-derivative. The position of nitrogroup in a benzene ring accompanied with an acylimide group is, as a rule, ortho- or more likely para-position in the reaction at ordinary temperatures. In the case of the nitration of centralite and also in the reaction between NO_2 gas and centralite, the easiest product is sym.-*p*-dinitrocentralite; and then, with regard to the structure of the compound in question, all possible cases of di- and tri-nitrocentralites, except meta-structures and extremely unsymmetrical nitrocompounds which are improbable, are only the following.

- (1) 4-4'-dinitro C/L. (Paraposition in a nucleus).
- (2) 2-2'-dinitro C/L., 2-6-2'-trinitro C/L. (Orthoposition in a nucleus).
- (3) 2-4-4'-trinitro C/L., 2-4-2'-trinitro C/L. (Ortho- and para-position in a nucleus).

A relationship between these chemical constitutions and absorption curves has been studied. Intensity of the absorption band in the case of ortho-compound is feeble and the form is not simple compared with para-compound as Figs. 4 and 5 show, while the unknown compound in question has simply a deep and wide absorption band. From this point, it is not possible to consider that it should be ortho-compound as the 2nd.

The hypochromic influence of two or three nitrogroups takes mutually metaposition from the same optical behaviours of 2-4-2'-4'-tetranitrocentralite (Fig. 2), 2-4-dinitrophenylurethane (Fig. 3), 2-4-6-trinitrobenzene,^w and 2-4-6-trinitroacetanilide (Fig. 4), so that the compound is not the 3rd type. There remains only the structure of the 1st type, in which each nitrogroup takes para-position for acylimide groups from the position of absorption band and its extinction coefficient, although it is not 4-4'-dinitrocentralite.

As for light absorption some para-nitro aromatic compounds with

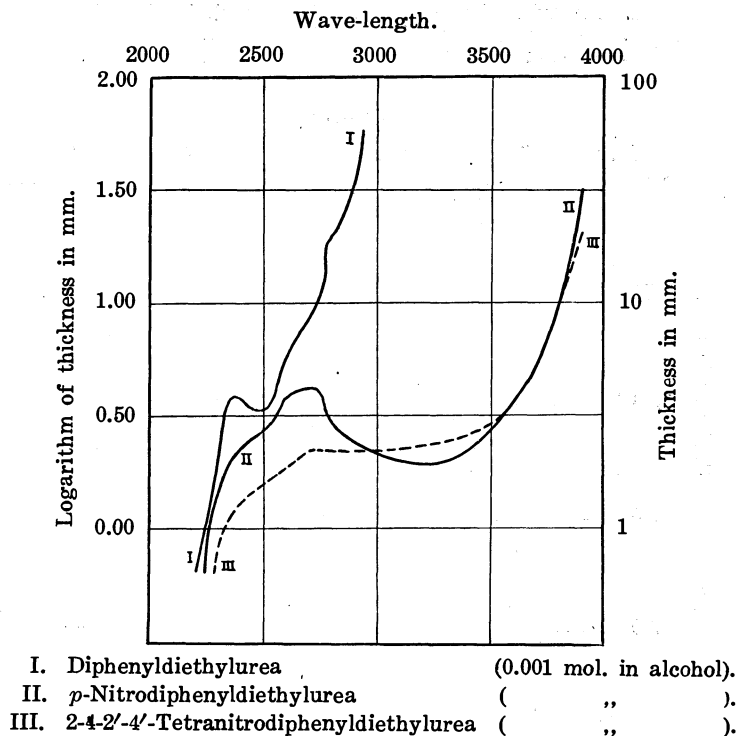
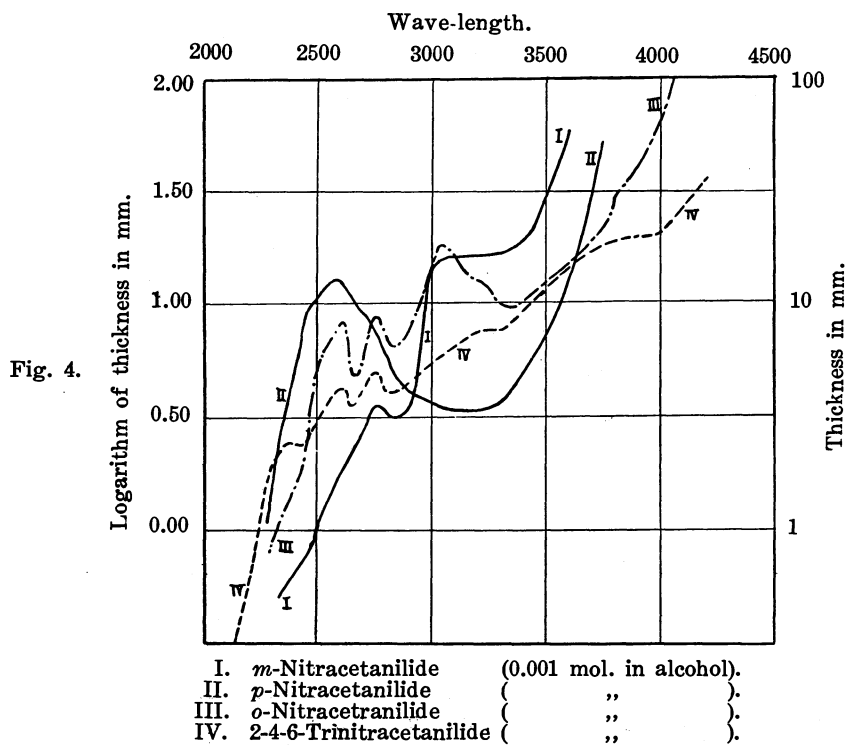
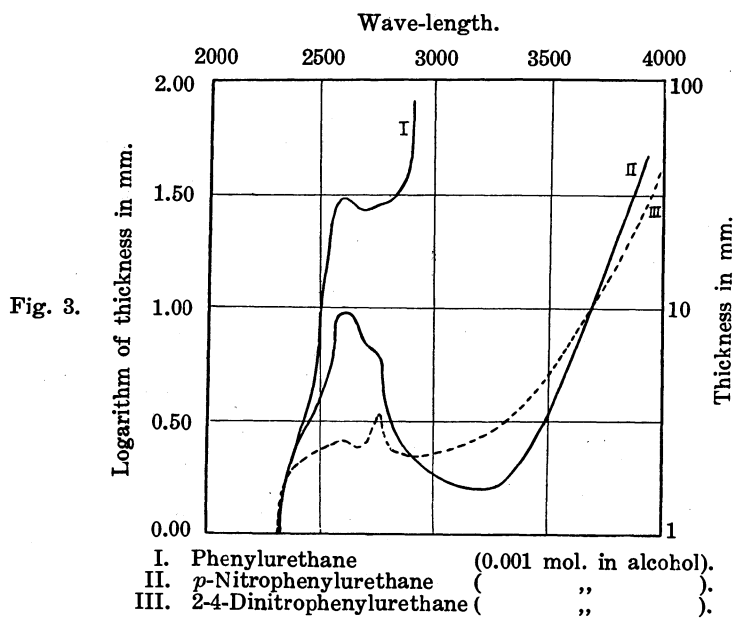


Fig. 2.

(1) *J. Chem. Soc.*, **103** (1913), 2085. *Ber.* **42** (1909), 2119; **43** (1910), 1662; **52** (1919), 493.



acylimide group are found to be almost the same as the following table shows.

	Wave length	log ϵ .
<i>p</i> -Nitroacetanilide	320 m. μ .	ca. 3.5
<i>p</i> -Nitrophenylurethane	320 "	" 3.8
Sym.- <i>p</i> -dinitro C/L	325 "	" 3.8
Unknown compound	335 "	" 3.8

These facts indicate that its formula is of a paranitro structure, and only small difference between unknown compound and dinitro C/L, which has more hypochromic influence than the former, may not be the influence of nitrogroup, but that of C_2H_5 -group when compared with *p*-nitroacetanilide and *p*-nitroethylacetanilide (Fig. 5). From the above considerations, the unknown compound might be dinitrodiphenylethylurea or dinitrodiphenylurea, one or two of ethyl-groups being expelled from dinitrocentralite. Checks and determinations have been carried out by measurements of molecular weight and microanalysis of elements in the constituents. By Rast's method, the following results have been obtained.

Camphor	Sample	Temp. depres.	Mol. wt.
0.0924 gr.	0.0044 gr.	7.6°C.	3.1×10^2
0.0889 gr.	0.0053 gr.	9.9°C.	3.0×10^2

These values being less than those of dinitrocentralite, the structure of which, excluding ethyl-group, is also probable, and there remains two cases as given below.

	Mol. wt.
Dinitrodiphenylethylurea	330
Dinitrodiphenylurea	302

The percentages of the elements of these compounds are the following.

Calc. for	C	H	N	O
Dinitrodiphenylethylurea ($C_{15}H_{14}N_4O_5$)	54.6	4.24	17.0	24.2
Dinitrodiphenylurea ($C_{13}H_{10}N_4O_5$)	51.6	3.32	18.5	26.5

The result of the analysis of the sample is given below.

Anal.: Subst. = 4.54; CO_2 = 9.05; H_2O = 1.98 mg.

Found: C = 54.3; H = 4.8; N = 16.6 %.

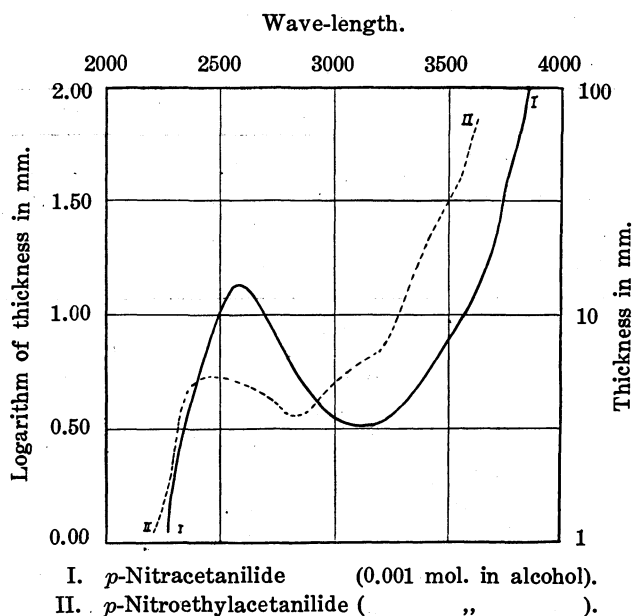
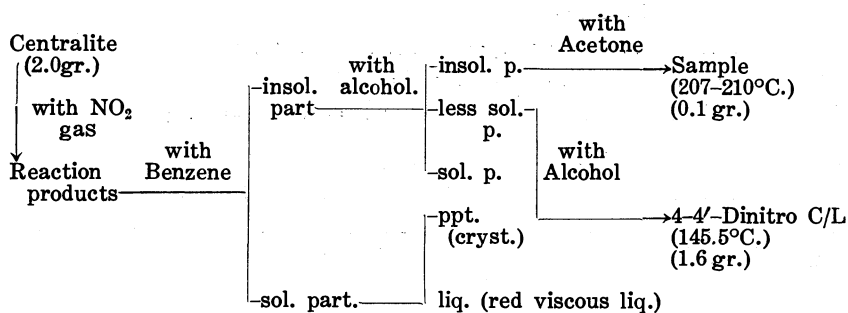


Fig. 5.

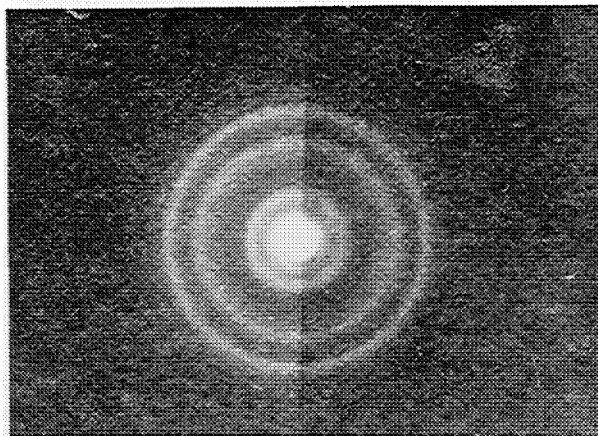
These are quite coincident with that of dinitrodiphenylethylurea. By these results and identification of that obtained by the synthesis which will be described later, the high melting point compound from centralite has been proved to be the dinitrodiphenyl-ethyl-urea.

Experimental Part.

Formation and Separation of the Sample. When NO_2 gas, diluted with air, was introduced in a bottle, containing 2.0 gr. of powdered centralite, the latter readily converted, from surface inward, into a viscous liquid of dark greenish colour, which turned brownish after allowing to stand overnight. This operation was repeated throughout a month or so, until no more reddish brown gas of NO_2 , remained unchanged, and the viscous liquid partially solidified. On the mass of the products, the fractional separation was carried out with benzene, then with alcohol, and 5% of the sample (0.1 gr.) was obtained from the insoluble part in benzene and the other part was almost dinitro-centralite that was 80% corresponding to the initial substance. The process of the separation is given in the following table.



Sample obtained from the part insoluble in benzene and in alcohol, crystallized from acetone solution, consisted of yellow very thin plate crystals melting at 207–210°C., while that obtained from alcohol was faintly greenish yellow powder before recrystallisation. It is hardly soluble in ordinary solvents, especially in benzene, slightly soluble in small amount in acetic acid and acetone. The X-ray photograph obtained by Debye's method is shown in the following figure.



X-ray photo. of unknown subs. $\times 0.7$
(Anticathode: Cu. dist. = 50 mm.)

Fig. 6.

4-4'-Dinitro-diphenyl-ethylurea. This substance was prepared by nitration of ethyldiphenylurea, which was obtained from phenylethylureachloride and aniline, at the temperature not exceeding 15°C. Twice recrystallisations with acetone suffice to render the raw product quite pure as crystals melting at 213.2–213.5°C.

Anal.: Subst. = 7.353; CO₂ = 14.62; H₂O = 3.26 mg.

Subst. = 1.921 mg.; N₂ = 0.287 c.c. at 23.0°C. and 775.3 m.m.

Found: C = 54.3; H = 4.9; N = 16.9%.

Calc. for C₁₅H₁₄N₄O₅: C = 54.6; H = 4.2; N = 16.9%.

Properties.—Very thin plate of yellow colour, insoluble or hardly soluble in ordinary solvents, only soluble in hot acetone. The absorption maximum was observed at 335 m.μ. Both in the absorption spectrum and X-ray photograph, the substance bears excellent resemblance to the sample obtained from C/L.

4-4'-Dinitrodiphenyldiethylurea. Centralite dissolved in glacial acetic acid was nitrated with nitric acid (sp. gr. 1.4) at a temperature not exceeding 15°C. and the product was crystallized from glacial acetic acid, then recrystallized from alcohol (M.P. 145.5°C.). In 0.001 mol alcoholic solution, the absorption maximum was observed at 325 m.μ.

2-4-2'-4'-Tetranitrodiphenyldiethylurea. This substance was obtained by nitration of centralite by conc. nitric acid (sp. gr. 1.5) at about 10°C. The product was crystallized from glacial acetic acid (M.P. 175°C.). In the 0.001 mol alcoholic solution, no absorption band was observed except an inflection in the absorption curve (Fig. 2).

Phenylurethane. The sample was prepared from aniline and diethylcarbonate which was obtained by the reaction between ethylalcohol and phosgene, COCl₂. The product melted at 51.5°C. The absorption maximum was observed at 269 m.μ. (Fig. 3).

p-Nitrophenylurethane.⁽¹⁾ By introducing nitric acid into etheric solution of phenylurethane, the sample was prepared (M.P. 127°C.), the absorption maximum of which was observed at 325 m.μ. (Fig. 3).

2-4-Dinitrophenylurethane.⁽²⁾ This substance was prepared by dissolution of phenylurethane in nitric acid (D. 1.5) at low temperature (M.P. 110–111°C.). In its absorption curve only slight maxima were observed at 268 m.μ. and 288 m.μ. (Fig. 3).

o-Nitracetanilide. m-Nitracetanilide. Both nitracetanilides were prepared from *o*-nitraniline⁽³⁾ or *m*-nitraniline⁽⁴⁾ and acetylchloride at ordinary temperature. The former melts at 92–93°C., and the latter

(1) *Ann.*, **233**, 9.

(2) *Rec. trav. chim.*, **10**, 141.

(3) *Ber.*, **39** (1906), 3903.

(4) *Ann.*, **57** (1846), 217.

at 145°C. These substances showed the following absorption maxima.

<i>o</i> -nitracetanilide	266 m. μ .	283 m. μ .	333 m. μ .
<i>p</i> -nitracetanilide		284 m. μ .	332 m. μ .

***p*-Nitracetanilide.**⁽¹⁾ ***p*-Nitroethylacetanilide.**⁽²⁾ By nitration of acetanilides, these two samples were obtained, the former melting at 207°C., the latter at 117–118°C. They show each a wide absorption band, the maximum of the former being observed at 321 m. μ ., while that of the latter at 285 m. μ . (Fig. 5).

2-4-6-Trinitroacetanilide.⁽³⁾ The substance was prepared from picramide and acetylchloride. It decomposed at 208–211°C.

Anal.: Subst. = 3.950 mg.; N₂ = 0.704 c.c. at 24.0°C and 766.1 m.m.

Found: N = 20.60 %. Calc. for C₇H₆N₄O₇: N = 20.68 %.

In its absorption curve four slight maxima were observed at 243 m. μ ., 265 m. μ ., 283 m. μ . and 311 m. μ . Three nitrogroups mutually in meta-positions in a benzene ring shows the hypochromic influence (Fig. 4).

In conclusion, the author wishes to express his gratitude to Prof. Y. Shibata for his suggestions and advice in connection with the spectrochemical part, to Prof. N. Yamaga for his interest in this work and to Mr. H. Marue for the trouble of taking the X-ray photographs.

Summary.

1. In 1926 M. A. Apard reported the formation of tetranitro-centralite by the reaction of nitric peroxide upon centralite at ordinary temperature. Owing to want of his experimental data, because of the very small quantity of his sample, it seemed however so doubtful that the author was tempted to set out this investigation, and determined its chemical structure by the spectrochemical and microanalytical methods.

2. Absorption spectra have been studied on the following ten substances. 4-4'-Dinitrodiphenyldiethylurea, 2-4-2'-4'-tetranitrodiphenyldiethylurea, *p*-nitrophenylurethane, 2-4-dinitrophenylurethane, *o*-nitroacetanilide, *m*-nitroacetanilide, *p*-nitroacetanilide, *p*-nitroethylacetanilide, 2-4-6-trinitroacetanilide and 4-4'-dinitroethyldiphenylurea.

(1) *Ber.*, **9**, 775. *Ann.*, **197**, 83.

(2) *Ber.*, **16**, 31. *Ber.*, **17**, 267.

(3) Compare *Ber.*, **41**, 3092.

3. As to the chemical constitution of the reaction product of higher melting point obtained from centralite, it has been proved to be dinitro-diphenylethylurea, which crystallizes from acetone solution in a form of very thin plates of yellowish colour, melting at 213.2–213.5°C., and hardly soluble in ordinary solvents.

Research Department, Naval Explosives Factory,
Hiratuka, Kanagawa.

A CONTRIBUTION TO THE FISH OIL THEORY OF
THE ORIGIN OF PETROLEUM FROM A STUDY
OF BRINE WATERS FROM WIDELY
DIFFERENT OIL FIELDS IN JAPAN.

By Tetsuya ISHIKAWA and Toshitomo BABA.

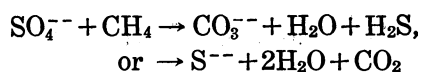
Received October 3rd, 1932. Published November 28th, 1932.

Introduction. The widely known fact that brine water and petroleum occur simultaneously in almost all of the oil fields in the world gives an interesting but unsolvable problem to scientists, but gives a cause of great annoyance to the workers of petroleum industry. Though no apparent relationship may exist between brine water and petroleum, yet their mysterious intimacy in nature tells us some intrinsic relation between them, and if this would be brought to light, the mystery concerning the origin of petroleum would probably be disclosed, and in consequence we would have some important clue which must be of great service to the discovery of petroleum deposit. This thought led some of the earlier petroleum geologists and chemists to their earnest studies of brines from different oil fields and to give rise to several theories of their origins. Prior to any other investigators, Hunt⁽¹⁾ in 1875 suggested from his study of the brine water from Ontario that it comes from the ancient sea water embedded simultaneously with the formation of the petroleum deposit. In 1905 Lane⁽²⁾ extended this idea more generally and published a well-known theory named the connate or fossil water theory, which states that the brine water from an oil field is no other than the ancient sea water secluded from the outer side and preserved in strata of earth. On the other hand, Washburne⁽³⁾ and Richardson⁽⁴⁾ have somewhat different opinions that the salts contained in brine water have not their origin in those

of the sea water as the forementioned investigators believed, but in some other salts which might come from easily soluble basic magmas or salt deposits. These opinions, however, do not seem to be adequate at least in Japan whose geological conditions differ from those in foreign countries. It may therefore be mentioned here that the acceptable theories at present are those which stand on sea water, though in particulars they are differently modified by many investigators.

Analyses of the Japanese Brine and the Discussion of Their Results.

The present authors who have had much interest in the co-existence of brine and petroleum for a long while had an opportunity to get the brines from widely different oil fields in Japan for which there have been little known in the literature. The brines taken for the analyses are those from the oil fields in Akita and Niigata Prefectures and that from the natural gas field with an oil indication in Chiba Prefecture. The results of the analyses are shown in Table 1, where the composition is given in molar ratios taking the sodium as 100%. Column 8 shows the absolute concentration of the sodium (grams per litre) in each brine for reference. Parallel to Table 1, Table 2 shows the composition of the sea waters from several places in the world which are all quoted from other authors. As seen from Table 1 and Table 2, it is clearly understood that the composition of sea waters give as already considered quite concordant values to each other independent of their occurring places, and that of brines are also, though not fairly concordant, yet roughly convergent to certain definite ratios in spite of the diversity in their geological distribution. Remarkable similarities are found between the composition of the sea water and that of the Japanese brine water in the ratios of the sodium, potassium and calcium, but far less quantities are observed in the magnesium and sulphate in the case of the brine, especially the latter being a trace or naught. The chlorine also seems to have somewhat lower values in the brine. As for the minute content of the sulphate in the brine from oil fields which is true not only for Japan, but also for any other countries, many explanations have been proposed by foreign investigators: Höfer⁽⁹⁾ and Rogers⁽¹⁰⁾ by whom the former's theory was supported, proposed that the lack of the sulphate may be due to the interaction between brine water and petroleum in the following chemical change:



The idea was rejected by Palmer⁽¹¹⁾ who stated that these reactions, being endothermic, can not be well explained unless some favorable con-

Table 1. Composition of Japanese brines.

Brines from	Na	K	Ca	Mg	Cl	SO ₄	Na	Authors
1 Innai, Akita Pref.	100	2.16	0.82	1.67	105.2	0.01	4.69	Ishikawa & Baba
2 Michikawa, Akita Pref.	100	0.21	5.34	5.31	110.8	0.01	6.00	„
3 Niizu, Niigata Pref. (Mean of 2 samples)	100	2.32 (3.02) (1.62)	1.16 (1.63) (0.68)	0.73 (1.15) (0.30)	79.1 (82.6) (75.6)	0.01 (0.02) (0.00)	4.40 (4.76) (4.03)	„
4 Nishiyama, Niigata Pref. (Mean of 4 samples)	100	0.32 (0.35) (0.27)	1.91 (2.62) (1.57)	0.49 (0.61) (0.40)	95.1 (101.7) (90.7)	0.00	6.72 (7.28) (6.16)	„
5 Ôtaki, Chiba Pref.	100	1.17	0.74	1.14	102.3	—	9.75	„
6 Katsurane, Akita Pref. (Mean of 6 samples)	100	2.42 (4.27) (1.09)	1.88 (6.70) (0.31)	0.96 (2.51) (0.30)	104.2 (117.4) (79.1)	0.12 (0.36) (0.02)	4.16 (8.05) (1.02)	Mikawa ⁽⁵⁾
7 Ôtaki, Chiba Pref. (Mean of 6 samples)	100	0.87 (1.96) (0.62)	0.77 (1.46) (0.23)	2.86 (4.53) (0.92)	89.0 (109.5) (54.6)	—	2.67 (6.40) (0.88)	Ôhashi ⁽⁶⁾

- (1) The Asahi Oil Co.'s well, 381.5–385.5 m. deep, at Innai-mura, Yuri-gun, Akita Prefecture.
 (2) The Asahi Oil Co.'s well, 162 m. deep, at Michikawa-mura, Yuri-gun, Akita Prefecture.
 (3) The Asahi Oil Co.'s well, 93 m. deep, of Aozawa, Take, Niizu-cho, Niigata Prefecture and the same Co.'s well, 270 m. deep, at Okubozawa, Take, Niizu-cho, Niigata Prefecture.
 (4) The Nippon Oil Co.'s wells, No. 33, 880 m. deep; No. 24, 771 m. deep; No. 60, 1200 m. deep; and No. 35, 1228 m. deep, at Taka-machi, Kariha-mura, Kariha-gun, Niigata Prefecture.
 (5) The Ôtaki Natural Gas Co.'s No. 2 well, at Oyamatsu, Fusamoto-mura, Isumi-gun, Chiba Prefecture.

Parentthesized figures show the highest and lowest values respectively.

Table 2. Composition of sea waters.

Seas	Na	K	Ca	Mg	Cl	SO ₄	Br	Na
Mean of 77 samples collected during the voyage of Challenger	100	2.12	2.25	11.50	117.2	6.02	0.176	10.77
Between Cape of Good Hope and England (Mean of 22 samples)	100	2.07	2.36	12.17	118.2	6.26	0.170	10.99
Near Carthage, Mediterranean	100	2.11	2.38	11.33	118.6	6.10	0.171	11.84
Black Sea (Mean of 6 samples)	100	2.24	2.66	11.61	117.3	5.87	0.170	6.17
Red Sea (Mean of 4 samples)	100	2.06	2.31	11.39	119.7	5.91	0.171	16.58
Genkai-Nada, Sea of Japan ⁽⁷⁾	100	2.18	2.35	11.33	114.9	5.96	—	10.11
Inland Sea, Japan ⁽⁸⁾	100	2.02	2.03	11.76	117.4	6.12	—	10.12

Table 3.
Composition of animal bloods (sera or plasmas).

Animals	Na	K	Ca	Mg	Cl	SO ₄	Authors
Medusa : Aurelia flavidula	100	3.05	2.37	10.81	120.3	3.79	Macallum ⁽¹⁴⁾
Horseshoe crab : Limulus polyphemus	100	3.31	2.33	10.59	121.3	3.83	„
Lobster : Homarus americanus	100	2.19	2.78	1.63	111.0	1.92	„
Sharks : Acanthias vulgaris	100	2.71	1.56	2.33	107.5	—	„
Mustelus canis	100	1.63	1.89	1.07	87.8	0.96	Smith ⁽¹⁵⁾
„	100	2.07	2.15	1.11	85.2	0.66	„
Carcharias littoralis	100	2.13	1.94	0.89	88.4	0.12	„
„	100	1.96	2.18	0.84	87.6	0.25	„
Rays : Raja stabuloforis	100	1.91	1.45	0.65	88.6	trace	„
„	100	1.91	1.23	1.02	97.5	trace	„
„	100	2.04	1.49	1.37	92.2	0.20	„
„	100	—	1.69	1.31	99.6	trace	„
Raja diaphenes	100	2.87	2.15	1.48	95.8	1.31	„
Fishes : Lophius piscatorius	100	3.48	1.74	0.50	95.0	0.60	„
„	100	3.76	2.10	8.07	112.4	1.99	„
„	100	4.39	1.02	0.68	81.0	1.76	„
„	100	3.42	1.09	—	89.1	1.14	„
Gadus callarias	100	2.72	2.78	2.11	87.8	—	„
„	100	5.59	2.26	1.33	97.1	—	Macallum ⁽¹⁴⁾
Pollachius virilus	100	2.55	1.78	1.38	89.4	—	„
Amia tatus calva	100	1.29	4.54	0.30	90.9	1.06	Smith ⁽¹⁵⁾
„	100	1.73	3.46	0.30	89.5	2.26	„
Lepidosteus osseus	100	1.93	4.36	0.21	84.3	1.71	„
Turtles : Chrysemys marginata	100	2.50	5.08	6.58	67.7	—	„
„	100	2.42	3.22	1.07	59.9	0.54	„
Graptemys geographia	100	1.94	2.74	0.40	69.8	0.32	„

Table 3.—(Concluded).

Animals	Na	K	Ca	Mg	Cl	SO ₄	Authors
Turtles: <i>Emys blandingii</i>	100	3.00	2.54	1.62	70.0	1.00	Smith ⁽¹⁵⁾
<i>Pseudemys elegans</i>	100	2.62	3.33	3.49	64.1	0.08	„
<i>Chelydra serpentina</i>	100	2.48	4.61	3.19	38.7	0.21	„
„	100	2.22	3.22	1.43	54.4	0.21	„
<i>Caretta kemp</i>	100	4.05	3.19	0.86	66.4	0.18	„
<i>Caretta caretta</i>	100	4.44	2.05	1.92	72.7	—	„
Dog	100	3.97	1.43	0.83	84.2	—	Abderhalden ⁽¹⁶⁾
„	100	3.49	1.47	0.72	82.4	—	„
Cat	100	3.89	1.37	0.75	82.0	—	„
„	100	3.94	1.24	0.87	66.1	—	Baumann & Kurland ⁽¹⁷⁾
Rabbit	100	3.84	1.45	0.80	76.0	—	Abderhalden ⁽¹⁶⁾
Ox	100	4.00	1.42	0.75	74.6	—	„
Pig	100	4.18	1.59	0.74	74.5	—	„
Horse	100	3.84	1.41	0.81	73.2	—	„
Man	100	3.42	1.71	0.86	69.2	1.37	Kramer & Tisdall ⁽¹⁸⁾

dition of thermochemical or geochemical action should occur.

Mills and Wells⁽¹²⁾ considered the diminution of the sulphate in the brine to be due to the adsorption of it by some colloidal particles charged with positive electricity.

Recently Bastin⁽¹³⁾ elucidated the same phenomenon by the action of micro-organisms whose metabolism necessarily consumes the sulphate in the brine.

Although the above explanations may prove the natural tendency of the unusual diminution of the sulphate in the brine, they can not interpretate the variation of the elements whose contents differ much from the contents in the sea water. In fact, little attention has been hitherto made in regard to the comparatively small content of the magnesium in the brine.

Taking the substantial differences between the sea water and the Japanese brine in consideration, the authors hesitate to accept the con-

nate water theory which necessitates the introduction of some other assumptions of different viewpoints in order to elucidate the fact. It must be remembered that a question whether or no the ancient sea water was possessed of the same composition as the contemporary one remains unsettled. This question is no doubt of interest from the geological and biological standpoints, but also of importance from the authors' viewpoint at the same time, as will be shown later on.

In 1910 Macallum⁽¹⁴⁾ put forward an interesting suggestion to this problem. He proposed, having analysed the inorganic constituents in the bloods of several animals (1) that the inorganic blood composition of an animal of a certain genus is entirely invariant ever since that genus took the first appearance on the earth and (2) that the inorganic blood composition of an animal created as an ancestor of a genus must be identical with that of the surrounding sea water at that time in order to be suited to environments. Table 3 shows the inorganic composition of blood sera or plasmas of various kinds of animals in the same expressions as taken in Table 1 and Table 2. The comparison of Table 3 with Table 2 which shows the composition of sea waters brings us that there exists some dissimilarity between them except the jelly-fish and horseshoe crab. The exceptional cases seen in the jelly-fish and horseshoe crab were regarded by Macallum as such, with a reason that they have incomplete excretory organs which admit sea water to pass through their bodies freely.

In the authors' opinion, however, his conception for the sea water of olden times seems to be wrong from the consideration of the paleontological fact that the jelly-fish appeared already in Cambrian formation and the horseshoe crab somewhat later but its larva quite resembles to the trilobite which appeared likewise in Cambrian, and it is highly probable to assume that the inorganic blood composition of these animals may indicate no other than the composition of the ancient sea water, and that that of the other animals which appeared far later than these have no such composition as that of the ancient sea water on account of their gradual development of organs.

It is also plausible from a geological standpoint of view that the composition of the ancient sea water did not differ so much from the to-day's so far as it is concerned to the sea water of a relatively new period such as Tertiary, when almost all of the petroleum deposits in Japan were formed.

From what has been stated above about the ancient sea water, the authors are convinced that the Japanese brine at least would not be

the same as the sea water in its origin, but something other as it will be discussed in the following.

Existing Theories of the Origin of Petroleum in Japan. Now it is a matter of great importance to look upon the theories hitherto published on the origin of petroleum in Japan which must be closely related to the origin of brine. Among the theories of the origin of Japanese petroleum the two theories are commonly accepted, one being proposed by Takahashi⁽¹⁹⁾ the other by Kobayashi.⁽²⁰⁾ According to Takahashi the organogenetic rocks which are found at oil strata in Japan may be the origin of petroleum because they always contain a minute quantity of kerosene often with a plenty of fossils of planktons, fishes and seaweeds, and these occurrence gave rôle of the formation of the brine water from the sea water whose composition differed little from the contemporary sea water. Although his idea for the brine water seems to surpass any other preceding theories in probable modification of the connate water theory instead of others' assuming the gradual transformation of the sea water into the brine with somewhat ambiguous changes, the brine as he considers is that which contains a large amount of alkaline earth elements such as the calcium and magnesium, whose phenomenon however is not the case in the Japanese brine as seen from Table 1. Kobayashi insisted on the so-called fish oil theory of the origin of the Japanese petroleum from the experimental facts of his own and coworkers i.e. fish oils yield petroleum-like hydrocarbons on dry distillation with Japanese acid clay at relatively low temperature and pressure. His theory is favorably accepted for the reason (1) that the distribution of the oil fields in Japan superposes approximately on that of the places producing acid clay and (2) that the oil fields can be considered to have situated at the seashores of the old times, where fishes were abundant. That the petroleum may be yielded from fish oils by the action of the acid clay only is not fully recognized, but that fish oils may be attributed to its origin is of some truth. In view of geological evidence most of Northern Honshu of Japan was yet unseen on the sea in the early Tertiary age and fishes propagated in abundance owing to hotter climate than that of to-day as it is easily imagined, when occurred subsequent revolutions on land and sea which caused fishes to gather⁽²¹⁾ near the seaside and to be buried under ground resulting in the formation of petroleum.

Grün and Wirth⁽²²⁾ who also supported the fish oil theory came to the conclusion that among fishes elasmobranchs are most probable as its origin because of the facts (1) that the livers of these fishes are

commonly large as compared with their bodies and contain a great amount, 70–90% of the total, of a higher terpentine-like hydrocarbon “squalene” named by Tsujimoto,⁽²³⁾ (2) that this yields hydrocarbons of great resemblance to natural petroleum by thermal decomposition and (3) that elasmobranchs were prosperous in the age of petroleum formation.

Independent of these investigators Tanaka and Kuwata⁽²⁴⁾ separated, with naphthenic acid, from the petroleum from Ishikari in Hokkaido, Niigata and Akita Prefectures some saturated fatty acids such as palmitic, myristic, stearic, and arachidic among which the first acid being predominant, and found that the relative amounts of these fatty acids are almost identical with those in whale oil, shark liver oil, herring oil, or cod oil. They claimed from these facts that the animals which are most probable as the origin of petroleum may be the shark or whale in consideration of their inhabitation.

To these concordant results obtained by different investigators which lay stress on the fish especially of elasmobranchs oil theory the present authors will add an important suggestion resulting directly from the analyses of the Japanese brine from oil fields.

Similarity in the Compositions of the Brine and of the Fish Blood.
The great resemblance between the composition of the Japanese brine and that of the bloods of fishes especially of elasmobranchs may be reasonably understood if we assume that the brine from an oil field comes from neither the sea water nor any underground water as the existing theories do, but from the body fluids of abundant corpses of fishes especially of elasmobranchs which are squeezed out by the compressive action of the earth crust, whose oily part being converted into petroleum at the same time.

The fact that the lack of the sulphate in the brine is simply explained by assuming as its origin elasmobranchs whose blood is lacking in the sulphate is of interest when we refer it to the rôle of sulphur compounds in the metabolism in the blood of higher animals. Indeed, elasmobranchs appeared already in Devon or Carboniferous ages while the other sea fishes in Jurassic and later ages.

According to Abderhalden⁽²⁵⁾ the inorganic composition of blood serum or plasma is not identical with that of blood corpuscle in the case of a higher animal such as the horse, pig, rabbit and man, and therefore it makes no estimation of the total inorganic blood composition from that of blood serum or plasma only. The blood corpuscles of these animals contain more potassium but less sodium than the blood sera or

plasmas which are shown in Table 3. As for a sea animal Macallum⁽¹⁴⁾ found that the total blood of the whale contains much potassium as the horse or pig does. Other higher animals such as the dog, cat, sheep, ox, deer, and etc., however, have no remarkable differences in the compositions of sera (or plasmas) and corpuscles, and such tendency would be the less, the lower an animal such as fish is. Smith's⁽¹⁵⁾ results indicated on this point that the body fluids of fishes are very similar in inorganic composition with their blood sera or plasmas. From the above elucidation, the authors' hypothesis that the Japanese brine would come from the blood of fishes especially of elasmobranchs may be easily accepted, consistent with the fish oil theories of the origin of petroleum proposed by Tanaka and Kuwata and by Grün and Wirth. But the whale taken as the origin by the former authors must be rejected from the above Macallum's result.

As it has been often reported⁽²⁵⁾ that a comparatively large amount of iodine and bromine were found in the analyses of brine waters, the authors have determined these contents as well as the other constituents already shown. The result are shown in Table 4, in which the contents of these elements in the sea water observed by Fellenberg⁽²⁶⁾ and etc. are also shown. As seen from this table the molar ratios of bromine of the brine and of the sea water have no difference between them, while the iodine of the former is from 500 to 3000 times as much as that

Table 4.

Iodine and bromine contents of the Japanese brine and of the sea water.

	Iodine	Bromine	Authors
Brine from Innai, Akita Pref.	0.096	0.27	Ishikawa & Baba
Brine from Michikawa, Akita Pref.	0.015	0.16	„
Brine from Niizu, Niigata Pref.	0.028	0.12	„
Brine from Nishiyama, Niigata Pref.	0.037	0.26	„
Brine from Ôtaki, Chiba Pref.	0.051	0.11	Ôhashi ⁽⁶⁾
Sea water	0.000031	0.17 (Mean, from Tab. 2)	Fellenberg ⁽²⁶⁾

Table 5.
Iodine content of bloods of mammals.

Mammals	Iodine content $\times 10^6$ gr. %	Authors
Man	11.0	Turner ⁽²⁷⁾
„	13	Kendall ⁽²⁷⁾
„	8–12.8	Veil & Sturm ⁽²⁸⁾
Dog	11.1	Turner ⁽²⁷⁾
Sheep	4.1–1.5	Mauer & Ducrue ⁽²⁹⁾
Rabbit	3.1–0.7	„

of the latter. The probable sources of such a considerable amount of iodine contained in the brines are perhaps due to marine lives, but the comparison of iodine content of the bloods of different animals with those of the brines can not unfortunately be done here because no appreciable data of fishes are found in the literature. In Table 5 the iodine content of a few mammals are given. Though somewhat low values are recorded in the cases of the sheep and rabbit, the iodine content of the bloods of mammals in general may be considered of the same order. Adopting the value 198 mg. % obtained by Kramer and Tisdall⁽¹⁸⁾ as one of the probable values for the absolute sodium content in the human blood, the molar ratio of the iodine to the sodium is calculated to be 0.0010, which is much greater than that of the sea water (0.000031) but still smaller than that of brines (0.015–0.096).

Now, for fishes no such comparison can be made, but it is a well-known fact⁽³⁰⁾ that fishes especially elasmobranchs contain richer iodine than any other higher animals do, and it is also evident from the study of Mauer and Ducrue⁽²⁹⁾ that their bloods are rich in iodine when considered their foods. As regards the bromine content in the animal bloods no much mention is possible, but according to Bernhardt and Ucko⁽³¹⁾ human blood contains from 1.0 to 1.5 mg. % in the normal state, which is equivalent to the molar ratio from 0.15 to 0.22, this indicating that the bromine content is perhaps universally constant in the animal bloods, the sea water and the brine.

If there is truth in what has been discussed for the origin of the brines, the brines from the same oil zone may have a constant or at least a similar composition with each other and conversely if under-

ground water has a composition of the known brine type, it may give an oil indication together with a help of geological inquiry. On this hypothesis, the authors have examined mineral waters widely occurring in Japan whose analyses were completely carried out by the Imperial Hygienic Laboratories.⁽³²⁾ Among more than five hundred kinds of hot or cold mineral waters they have picked up three kinds of cold waters very similar to the brine type, whose composition is shown in Table 6 in the same expressions as before: The first is at Nagano in Niigata Prefecture, situated near Ômo, a famous oil field in the same Prefecture, the second is at Onishika, situated within the circumscription of the well-known Rumoi oil field in Teshio of Hokkaido. These two must of course be included in the same type of the brines shown in Table 1. The third is at Kashio in Nagano Prefecture where there has had as yet no production of petroleum, but an oil indication is beyond question according to the generally accepted geological opinion that it is situated on the famous Itoigawa-Shizuoka fault line, along which may exist the elongation of the great petroleum zone of northern part of Japan.

Table 6.

Composition of mineral waters of the brine type in Japan.

Mineral waters from	Na	K	Ca	Mg	Cl	Br	I	SO ₄
1 Nagano, Niigata Pref.	100	0.55	1.77	3.18	100.7	0.10	0.010	0.015
2 Onishika, Hokkaido	100	0.93	3.50	2.37	105.8	0.11	0.034	—
3 Kashio, Nagano Pref.	100	0.83	3.25	0.66	108.9	0.04	trace	trace

NOTE:

- (1) Nagano, Morimachi-mura, Minamikambara-gun, Niigata Prefecture.
- (2) Onishika-mura, Rumoi-gun, Teshio Province, Hokkaido.
- (3) Kashio, Oshika-mura, Shimoina-gun, Nagano Prefecture.

Conclusion. From the above results the authors have come to the conclusion that the Japanese brine from oil fields have a certain type of composition which is remarkably similar to the inorganic blood composition of fishes, especially of elasmobranchs and that this fact can be reasonably explained by assuming that the origin of the brine from oil fields are the body fluids of these fishes whose oils have been known to be most plausible as the origin of petroleum. Though the mechanism of the formation of petroleum as well as of brine water from the corpses of these fishes can not be fully accounted for, the above considerations will be of service to the investigation in the line.

The authors wish to express their sincere thanks to Dr. M. Ôkôchi, head of the Institute of Physical and Chemical Research in Tokyo who has encouraged them with much interest throughout the present study, to Mr. T. Hidaka, chief staff of the mining section of the Asahi Oil Co. and also to Mr. T. Yoshimura, chief of the Kashiwazaki Laboratory of the Nippon Oil Co. by whom the samples were offered to them, and to Mr. I. Mikawa from whom they received a valuable reference paper.

Literature.

1. T. S. HUNT, *Chemical & Geological Essays*, Boston, (1875), 117.
2. A. C. LANE, *J. Geol.*, **14** (1905), 221; *Geol. Soc. Am. Bull.*, **19** (1908), 501.
3. C. M. WASHBURNE, *Am. Inst. Eng. Trans.*, **48** (1904), 687.
4. G. B. RICHARDSON, *Econ. Geol.*, **12** (1917), 37.
5. I. MIKAWA, *J. Geol. Soc. Tokyo*, **37** (1930), 639.
6. T. OHASHI, *J. Geogr. Tokyo*, **34** (1922), No. 408.
7. T. MAEDA, *J. Soc. Chem. Ind., Japan*, **23** (1920), 1131.
8. U. SHIMADA, *Sci. Papers, Centr. Research, Inst. Jap. Gov. Monopoly Bureau*, (1925).
9. H. v. HÖFER, *Das Erdöl*, II (1909), 28.
10. G. S. ROGERS, *U.S. Geol. Surv. Bull.*, (1917), 653; *U.S. Geol. Surv., Prof. Paper*, (1919), 117.
11. C. PALMER, *Econ. Geol.*, (1924), No. 7.
12. V. R. MILLS & R. C. WELLS, *U.S. Geol. Surv. Bull.*, (1919), No. 693.
13. E. S. BASTIN, *Bull. Am. Assoc. Petr. Geologists*, **10** (1926), No. 12.
14. A. B. MACALLUM, *Proc. Roy. Soc. London*, B **82** (1910), 602.
15. H. W. SMITH, *J. Biol. Chem.*, **81** (1929), 412; **82** (1929), 73, 653.
16. E. ABDERHALDEN, *Z. Physiol. Chem.*, **25** (1898), 106; *Chem. Zentr.*, II **69** (1898), 43.
17. E. J. BAUMANN & S. KURLAND, *Z. Physiol. Chem.*, **71** (1926-27), 284.
18. B. KRAMER & F. F. TISDALL, *Z. Physiol. Chem.*, **53** (1922), 248.
19. J. TAKAHASHI, *Sekiyu Kosho Shinron* (New Theory of Petroleum), (1922).
20. K. KOBAYASHI, *J. Soc. Chem. Ind., Japan*, **24** (1921), 1; *J. Soc. Chem. Ind.*, **40** (1921), 250 A; *Sekiyu oyobi sono Kogyo* (Petroleum and its Industry), II (1928), 149.
21. T. TERADA, "Earthquakes and Fisheries," *Proc. Imp. Acad. Tokyo*, **8** (1932), 83.
22. A. GRÜN & T. WIRTH, *Ber.* **53** (1920), 1301.
23. M. TSUJIMOTO, *J. Soc. Chem. Ind., Japan*, **9** (1906), 953; *Ind. Eng. Chem.*, **8** (1916), 889; **9** (1917), 1098.
24. Y. TANAKA & T. KUWATA, *J. Soc. Chem. Ind., Japan*, **32** (1929), 1.
25. For example, K. Krejci-Graf, *Grundfragen der Oelgeologie, Brennstoff-Geologie*, (1930), 4.
26. TH. v. FELLEBERG, *Biochem. Z.*, **152** (1924), 116.
27. R. G. TURNER, *J. Biol. Chem.*, **88** (1930), 497.
28. W. H. VEIL & A. STURM, *Deutsch Arch. Klin. Med.*, **147** (1925), 166.
29. E. MAUER & H. DUCRUE, *Biochem. Z.*, **193** (1928), 368.
30. A. T. CAMERON, *J. Biol. Chem.*, **18** (1914), 335; TH. v. FELLEBERG, *Biochem. Z.*, **139** (1923), 444; *Tablae Biologie*, Berlin, VII (1925), 300.
31. H. BERNHARDT & H. UCKO, *Biochem. Z.*, **155** (1925), 174.
32. A Table of Composition of Mineral Waters in Japan, *Bull. Imp. Hygienic Laborat.*, **34** (1929).

EINFLUSS DES NATRIUM-, BARIUM- UND ALUMINIUM- CHLORIDS AUF DIE HYDROLYSE DES EISENCHLORIDS BEI ÜBER 100°C.

Von Tominosuke KATSURAI.

Eingegangen am 18. Oktober 1932. Ausgegeben am 28. November 1932.

Die Hydrolyse des Eisenchlorids bei über 100°C wurde schon von verschiedenen Autoren untersucht, aber die Änderung der Hydrolyse des Eisenchlorids durch Anwesenheit von Fremdsubstanzen scheint noch nicht studiert zu sein. Als ein einfaches Beispiel zu diesen Fällen beobachtete ich die Reaktion, die bei Erhitzung der drei Mischungen, (A) $\text{FeCl}_3 + \text{NaCl}$ (B) $\text{FeCl}_3 + \text{BaCl}_2$ und (C) $\text{FeCl}_3 + \text{AlCl}_3$, auf über 100°C stattfindet. NaCl , BaCl_2 und AlCl_3 wurden als Repräsentanten der uni-, di- und trivalenten Verbindung ausgewählt.

In der vorliegenden Arbeit wird der schon in einer früheren Abhandlung beschriebene Autoklav angewendet.⁽¹⁾ Nachdem die gewünschte Temperatur darin erreicht ist, wird das Erhitzen noch eine Stunde fortgesetzt. Über das Verfahren ist auch schon damals Genaueres gesagt worden. Die Mischung wird so hergestellt, dass die Konzentration der beiden Substanzen in (A), (B) und (C) 0.25N ist, z.B. besteht die Mischung (A) aus je 10 ccm 0.5N FeCl_3 und 0.5N NaCl . Für jede Mischung ist neu hergestellte Lösung des Eisenchlorids angewendet worden.

Dabei ist ein Platintiegel von einem Volumen von ca. 25 ccm mit Platindeckel benutzt worden, in der Annahme, dass das Platin für den vorliegenden Versuch am zweckmässigsten sei. Eine schematische Skizze des Autoklavs mit Untersatz für den Platintiegel ist in der folgenden Figur gegeben. Die Mischungen (A), (B) und (C) wurden bei 120°, 140° und 160°C geprüft.

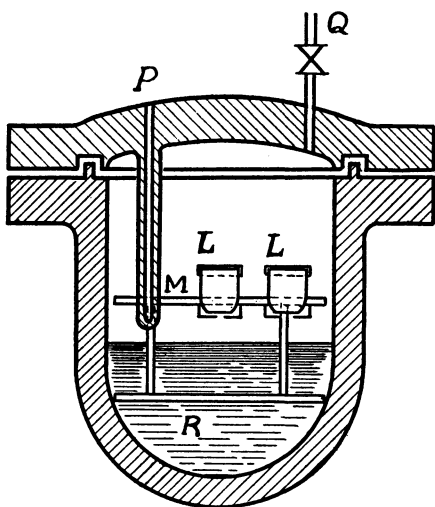
(A) 0.25N in FeCl_3 und in NaCl und (B) 0.25N in FeCl_3 und in BaCl_2 .

Bei 120°C und noch bei 140°C sedimentierte gelber Niederschlag auf dem Boden des Tiegels. Es ist erst bei 160°C gelungen, hämatitähnlichen Niederschlag zu erhalten.

(C) 0.25N in FeCl_3 und in AlCl_3 .

Schon bei 140°C fand der hämatitähnliche Niederschlag statt. Die

(1) T. Katsurai u. T. Watanabe, *Sci. Pap. Inst. Phys. Chem. Research*, **13** (1930), 89.



Querschnitt des Autoklavs.

Skala : ca. $\frac{1}{5}$ der natürl. Grösse

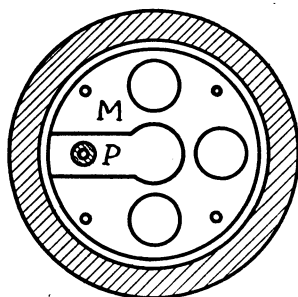
L: Platintiegel

M: Untersatz

P: Höhlung für den Thermometer

Q: Hahn

R: Wasser



Lösung 0.25N FeCl_3 zerfiel auch bei 140°C in Hämatit (Fe_2O_3) mit HCl , wovon das erstere auf dem Boden sedimentierte und das letztere den oberen klaren flüssigen Teil bildete.⁽¹⁾ Bei 160°C zeigten 0.25N BaCl_2 und auch 0.25N AlCl_3 keine Spur des Zerfalls.

Zusammenfassung.

Es wurde der Einfluss des NaCl , BaCl_2 und AlCl_3 auf die Hydrolyse des FeCl_3 bei über 100°C studiert. Dabei wurde beobachtet, dass NaCl und BaCl_2 die Hydrolyse störten, d.h. die notwendige Temperatur für den vollkommenen Zerfall des FeCl_3 erhöhte sich durch die Anwesenheit dieser Substanzen. Das AlCl_3 übte bei der Hydrolyse des FeCl_3 keinen merkbaren Einfluss auf die Temperatur aus.

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

STUDIES ON MOLECULAR-REARRANGEMENTS OF
 α -GLYCOLS. VI.
 RELATIVE ELECTRONEGATIVITIES OF *p*-ANISYL
 AND NAPHTHYL RADICALS.

By Masao MIGITA.

Received October 27th, 1932. Published December 28th, 1932.

In the earlier literatures naphthyl radicals are conceived to be the most electronegative radicals. Thus Skraup⁽¹⁾ has obtained the result that naphthyl radicals have the highest "affinity requirement" and *p*-anisyl radical is next to them, when he has compared so called affinity requirement of organic radicals by his "oxazol-" and "carbinol-" methods. It has been already discussed that the "affinity requirement" is nothing but electronegativity.⁽²⁾

Establishing the relative electronegativities of organic radicals by double decomposition of unsymmetrical organomercuric compounds and hydrogen chloride, Kharasch and Marker⁽³⁾ have given the result that naphthyl radicals rank first and *p*-anisyl radical comes next. But later, after closer experiments, the following correction was made for this order that *p*-anisyl radical is the most negative and α -naphthyl radical is the second.⁽⁴⁾

It will be interesting to check these results by determining the relative electronegativities of *p*-anisyl and naphthyl radicals by some other method. For this purpose, we can find an excellent method in the rearrangements of symmetrical pinacones, which has been proposed by the author with its theoretical deduction, and its applicability has been proved by a series of experimental data.⁽⁵⁾

As for α -naphthyl radical, Bailar⁽⁶⁾ calculated its migration tendency with respect to *p*-tolyl and *p*-anisyl radicals, in the rearrangements of sym. di-*p*-tolyl-di- α -naphthyl glycol and sym. di-*p*-anisyl-di- α -naphthyl glycol, and found that taking the migration tendency of α -naphthyl radical 1, those of *p*-tolyl and *p*-anisyl radicals are 0.88 and 2 respectively. This Bailar's result can be interpreted from the author's theory as follows: α -naphthyl

(1) Skraup, *Ber.*, **55** (1919), 1080, 1074.

(2) Migita, this Bulletin, **7** (1932), 342 foot-note.

(3) Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130.

(4) Kharasch and Reinmuth, *J. Chem. Education*, **5** (1928), 408.

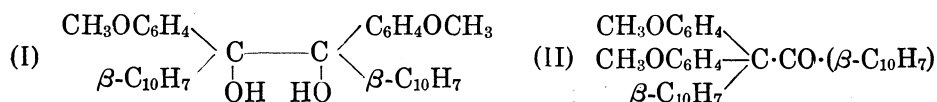
(5) Migita, this Bulletin, **7** (1932), 341.

(6) Bailar, *J. Am. Chem. Soc.*, **52** (1930), 3596-3603.

radical is somewhat more negative than *p*-tolyl radical and fairly more positive than *p*-anisyl radical.

As little has been known of electronegativity of β -naphthyl radical, intending to determine the rank of this radical in the series representing relative electronegativities of organic radicals by the pinacoline method, the rearrangement of sym. di-*p*-anisyl-di- β -naphthyl glycol (I) was first studied.

In the actual rearrangement of this glycol (I) migration of anisyl radical takes place exclusively, di-*p*-anisyl- β -naphthyl- β -naphthoyl methane (II) being produced, which shows that *p*-anisyl is by far more negative than β -naphthyl radical, conforming with the result given by Kharasch and Reinmuth in the later paper.



It is interesting that migration of α -naphthyl radical takes place, though to a lesser extent, as well as *p*-anisyl radical, in the rearrangement of sym. di-*p*-anisyl-di- α -naphthyl glycol, while in the case of sym. di-*p*-anisyl-di- β -naphthyl glycol, migration of *p*-anisyl radical nearly exclusively occurs. Because these results lead us to the inference that α -naphthyl is more negative than β -naphthyl radical, since in the rearrangement of a symmetrical pinacone, the two substituents migrate with different aptitudes, namely, the more negative radical has the greater migratory aptitude, and migration of one radical takes place exclusively, when the electronegativities of the two substituents are widely different, as discussed in the last paper.⁽¹⁾

Sym. di-*p*-anisyl-di- β -naphthyl glycol is obtained by reducing *p*-anisyl- β -naphthyl ketone by glacial acetic acid and zinc dust at room temperature. The corresponding pinacoline (II) is obtained by the action of acetyl chloride on the pinacone or simply by heating the pinacone with acetic acid. Therefore, the reduction of the ketone by glacial acetic acid and zinc dust at higher temperature gives the pinacoline as in the case of di-anisyl ketone and *p*-methoxy-*p*'-ethoxy-benzo-phenone.⁽²⁾ Here we can find another instance of increase of reactivity of a pinacone caused by highly negative substituents in the molecule.

When *p*-anisyl- β -naphthyl ketone was reduced by absolute alcohol under direct sunlight, change of its crystalline form was observed from thick prisms to thin leaflets, but the ketone remained unchanged.

(1) Loc. cit.

(2) Migita, this Bulletin, 7 (1932), 338, 343.

Experimental Part.

***p*-Anisyl- β -Naphthyl Ketone**, $p\text{-CH}_3\text{OC}_6\text{H}_4\cdot\text{CO}\cdot\beta\text{-C}_{10}\text{H}_7$. The ketone was prepared from β -naphthoyl chloride (19.0 gr.) and anisole (12 gr.) by Friedel-Crafts' reaction. The reaction proceeded smoothly and after usual steam treatment, dark coloured buttery mass was obtained which could be purified either from hot ligroin or hot alcohol. From ligroin it crystallised in an aggregate of slightly coloured prisms, while from the latter it crystallised in white scales with pearly lustre. When recrystallised from alcohol, it crystallises in scales or needles depending on conditions and melts at 93°C . It dissolves in concentrated sulphuric acid with orange colour. The yield of the pure product amounted to 14 gr. which represents 54 % of the theory.

Anal.: Subst. = 0.0685; CO_2 = 0.2067; H_2O = 0.0342 gr.

Found: C = 82.3; H = 5.59%.

Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_2$ (Ketone): C = 82.5; H = 5.59%.

Sym. Di-*p*-Anisyl-di- β -Naphthyl Glycol,

$$\begin{array}{c} (p\text{-CH}_3\text{OC}_6\text{H}_4)(\beta\text{-C}_{10}\text{H}_7)\text{C}(\text{OH}) \\ | \\ (p\text{-CH}_3\text{OC}_6\text{H}_4)(\beta\text{-C}_{10}\text{H}_7)\text{C}(\text{OH}) \end{array}$$

2.3 Gr. of *p*-anisyl- β -naphthyl ketone were dissolved in sufficient glacial acetic acid (ca. 50 c.c.) to keep it in solution at room temperature, to which 10 gr. of zinc dust were added, allowing the mixture to stand at room temperature for five days. White precipitates which fell over zinc dust, were filtered, boiled with ether to remove impurities and finally recrystallised from benzene and petroleum ether. It melts at 160°C ., and dissolves in concentrated sulphuric acid with dark brown colouration which assumes gradually reddish tint. It is almost insoluble in alcohol and ether. The yield was about 0.5 gr. By boiling the unchanged zinc dust with benzene, a further quantity of the glycol was obtained.

Anal.: Subst. = 0.0634; CO_2 = 0.1906; H_2O = 0.0345 gr.

Found: C = 82.1; H = 6.11%.

Calc. for $\text{C}_{36}\text{H}_{30}\text{O}_4$ (Pinacone): C = 82.2; H = 5.71%.

When the acetic acid solution from which the pinacone and unchanged zinc dust were filtered off, was poured into water, white precipitates were obtained, which, however, when purified from benzene and petroleum ether, produced only syrupy substance, which dissolves in organic solvent with yellow colour.

Rearrangement. The pinacone was boiled with acetic acid for 10 minutes and poured into water. Resulting white flocculent precipitates

were recrystallised from ether. The product melts at 185°C. with frothing. No depression of melting point was observed, when mixed with di-*p*-anisyl- β -naphthyl- β -naphthoyl-methane, prepared by reducing the ketone with boiling acetic acid and zinc dust (See below). The yield was nearly quantitative.

By treating the pinacone with acetyl chloride and glacial acetic acid in benzene solution, the same result was obtained.

Di-*p*-Anisyl- β -Naphthyl- β -Naphthoyl-Methane,



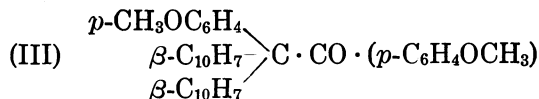
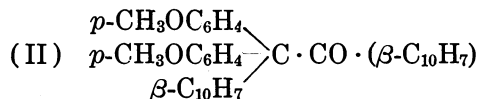
To gently boiling solution of *p*-anisyl- β -naphthyl ketone (5.2 gr.) in glacial acetic acid (24 c.c.), 12 gr. of zinc dust were added by portions. Slightly yellowish precipitates which were obtained by pouring the reaction products into water, were drained and dissolved in ether. When this ethereal solution was boiled gently, white crystalline powder gradually precipitated, being freed from impurities which remained in solution. The product, purified from chloroform and ether, melts at 185°C. with frothing. It is nearly insoluble in ether, only sparingly in hot ligroin and alcohol, readily soluble in chloroform, acetic acid and hot benzene. It dissolves in concentrated sulphuric acid with brownish black colour, which assumes gradually reddish tint.

Anal.: Subst. = 0.0754; CO_2 = 0.2346; H_2O = 0.0387 gr.

Fonnd: C = 84.8; H = 5.75%.

Calc. for $\text{C}_{36}\text{H}_{28}\text{O}_3$ (Pinacolone): C = 85.1; H = 5.51%.

Constitution. The constitution of this pinacolone is either of the two possible isomers, II and III, which give, by hydrolysis, β -naphthoic acid and *p*-anisic acid respectively.



Though these two acids have close melting points, they can be easily distinguished by their solubilities in water and in ligroin and by the optical properties of the crystals (See the following table).

	β -Naphthoic acid.	<i>p</i> -Anisic acid.
M. P.	184°C.	182°C.
Optical properties.	Monoclinic prisms, elongation positive for crystals with straight extinction.	Monoclinic prisms, elongation negative for crystals with straight extinction.
Solubility in hot water.	Very difficultly.	Moderately.
Solubility in hot ligroin.	Recrystallisable.	Only in trace.

2 Gr. of the pinacoline were boiled with 100 c.c. of 20% alcoholic potash. The pinacoline which is insoluble in hot alcohol, passed gradually into solution as the hydrolysis proceeded. After about twenty hours a clear solution was obtained, which, however, was kept boiling further for six hours. Alcohol was expelled under reduced pressure, acidic and neutral constituents being isolated by usual method.⁽¹⁾

The acidic product which was insoluble in hot water, was dissolved in a quantity of hot ligroin. On cooling the solution, it was obtained in the form of slightly coloured fine needles, which were recrystallised from ligroin with an addition of animal charcoal. It melted at 184°C., and was identified as β -naphthoic acid by mixed melting point test and by the optical properties of the crystals.

The neutral constituent was obtained as dark coloured syrup which was deemed impossible to be brought into crystallisation. However, the author has succeeded in obtaining thick prisms by leaving it to stand at room temperature for two months. The crystals, purified with ether on porous plate, melted at 89–90°C. with frothing and solidified in a glassy mass. Its composition was coincident with that of di-*p*-anisyl- β -naphthyl-methane, $(p\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{CH}(\beta\text{-C}_{10}\text{H}_7)$.

Anal.: Subst. = 0.0648; CO_2 = 0.2010; H_2O = 0.0385 gr.

Found: C = 84.6; H = 6.63%.

Calc. for $\text{C}_{25}\text{H}_{22}\text{O}_2$: C = 84.7; H = 6.21%.

Thus it has been proved that in the rearrangement of sym. di-*p*-anisyl-di- β -naphthyl glycol, migration of *p*-anisyl radical took place exclusively and the pinacoline, produced, has the constitution of formula II.

Reduction by Absolute Alcohol under Direct Sunlight. Two grams of *p*-anisyl- β -naphthyl ketone were sealed in a tube with about 50 c.c. of

(1) Migita, this Bulletin, 7 (1932), 344.

absolute alcohol and exposed to direct sunlight for a month. After the end of the first week, change of crystalline form was observed from thick prisms to thin leaflets. On opening the tube, however, formation of acetaldehyde was detected neither by smell nor by Schiff's reagent. The leaflets were filtered and recrystallised from alcohol. It melted at 93°C . and dissolved in concentrated sulphuric acid with orange colour. It was identified as the original ketone by mixed melting point test.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

STUDIES ON MOLECULAR-REARRANGEMENTS
OF α -GLYCOLS. VII.
RELATIVE ELECTRONEGATIVITIES OF β -NAPHTHYL
AND DIPHENYLYL RADICALS.

By Masao MIGITA.

Received October 27th, 1932. Published December 28th, 1932.

As for the dissociation degree of hexa-aryl ethanes, it is known that diphenylyl radical is more potent than phenyl, and naphthyl radicals are more potent than diphenylyl in causing the increase of dissociation of hexa-aryl ethanes. Thus, hexaphenyl ethane, tetraphenyl-bis-diphenylyl ethane, tetraphenyl-di- β -naphthyl ethane and tetraphenyl-di- α -naphthyl ethane dissociate into the corresponding monomers to 0%, 15%, 30% and 60% respectively.⁽¹⁾ According to the electronic conception of valency, instability of a carbon-to-carbon bond is attributed to the displacement of the binding electrons from one or both bound carbon atoms. Then, the increase of negativities of the substituents of a hexaaryl ethane will lead to the increase of dissociation of the ethane-molecule, since it causes the decrease of the negativities of the two adjacent carbon atoms in chain; in other word, it causes the increase of displacement of the binding electrons from the both carbon nuclei. Consequently, under certain conditions, it may be admitted to compare electronegativities of the substituents of hexa-aryl ethanes by their dissociation degree. Hereby, the above mentioned radicals will be in the following order with respect to their electronegativities: α -C₁₀H₇ > β -C₁₀H₇ > C₆H₅.C₆H₄ > C₆H₅.

(1) Gomberg, *Chem. Rev.*, **1** (1925), 104.

In the recent papers dealing with the rearrangements of symmetrical aromatic pinacones, we can find some data concerning the migration tendency of diphenyl radical with respect to some radicals in the pinacoline rearrangements (Table 1).

TABLE 1.

$\begin{array}{c} \text{R} \quad \text{R} \\ \text{C}_6\text{H}_5\text{-C}_6\text{H}_4\text{-}\dot{\text{C}}\text{---}\dot{\text{C}}\text{-C}_6\text{H}_4\text{-C}_6\text{H}_5 \\ \text{OH} \quad \text{HO} \end{array}$	Migration aptitudes.		Observers.
R	$\text{C}_6\text{H}_5\text{-C}_6\text{H}_4$.	R.	
C_6H_5	96.5%.	4.5%.	Gomberg and Bachmann. ⁽¹⁾
$p\text{-BrC}_6\text{H}_4$	92.0%.	8.0%.	Gomberg and Bailar. ⁽²⁾
$p\text{-CH}_3\text{C}_6\text{H}_4$	43%.	57%.	Bachmann and Moser. ⁽³⁾
$p\text{-CH}_3\text{OC}_6\text{H}_4$	3.2%.	96.8%.	

It will be inferred from these results that diphenyl radical is by far more electropositive than p -anisyl radical, and slightly more positive than p -tolyl radical, but exceedingly electronegative than phenyl and p -bromophenyl radicals, since according to the author's theory,⁽⁴⁾ the migratory tendencies of the substituents of a symmetrical pinacone can be taken for a criterion of their electronegativities.

In the present work, rearrangement of sym. di- β -naphthyl-bis-diphenyl glycol has been studied, intending, on the one hand, to make a supplement to the series representing relative electronegativities of organic radicals by determining the relative positions of β -naphthyl and diphenyl radicals in the series by the pinacoline method, and on the other hand, to check, thereby, the result inferred from the dissociation degree of hexa-aryl ethanes.

On hydrolysing the rearrangement product of this pinacone, both β -naphthoic acid and p -phenyl-benzoic acid were obtained with slightly different yields, namely, the former with somewhat better yield than the latter. However, taking into consideration the remarkable difference in the easiness with which the two parent pinacolines are hydro-

(1) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 251.

(2) Gomberg and Bailar, *ibid.*, **51** (1929), 2237.

(3) Bachmann and Moser, *ibid.*, **54** (1932), 1127.

(4) Migita, this Bulletin, **7** (1932), 341.

lysed (see p. 387), migration of β -naphthyl and diphenyl radicals may be taken to occur nearly to an equal extent; in other words, there is no marked difference between these two radicals with respect to their electronegativities. Thus, the result obtained is not consistent with that inferred from the dissociation degree of tetraphenyl-di- β -naphthyl and tetraphenyl-bis-diphenyl ethanes. Though it can not be decided simply which of these results is more probable, the author wishes to place more weights upon the pinacolone method, since the hexa-aryl ethane method has often given deviated results,⁽¹⁾ probably owing to the fact that the dissociation degree of hexa-aryl ethanes depends not only on the negativities of substituents, but also on the experimental conditions, such as concentration, temperature and the solvent in which the dissociation takes place.

Sym. di- β -naphthyl-bis-diphenyl glycol was prepared by reducing β -naphthyl-diphenyl ketone with magnesium and magnesium iodide, while reduction of this ketone to the pinacone by other methods was proved unsuccessful.

Reduction of this ketone by zinc dust and glacial acetic acid is a subject of some interest, since it produced the corresponding methane at higher temperature, and the carbinol at room temperature.

The ketone remained unchanged by the action of alcohol under direct sunlight.

Experimental Part.

β -Naphthyl-Diphenyl Ketone. β -C₁₀H₇.CO.C₆H₄.C₆H₅. This ketone was prepared from β -naphthoyl chloride and diphenyl by Friedel-Crafts' reaction, where the formation of the by-product, di-naphthoyl diphenyl, was avoided after Montagne's modification⁽²⁾ employed in the preparation of phenyl-diphenyl ketone. 14.2 Gr. of the acid chloride and 12 gr. of aluminium chloride were warmed in 65 c.c. of carbon-bisulphide, to which were added, on cooling, 20 gr. of diphenyl (twice its equivalent quantity), and warmed on water bath. After twenty hours' heating, the aluminium complex was hydrolysed and the resulting yellowish-brown crystalline cakes were subjected to usual steam treatments. The raw products, after digestion with a small bulk of ether to remove coloured impurities, were crystallised from acetone with an addition of animal

(1) For example, the dissociation degree of tetraphenyl-di-*p*-anisyl ethane is only about 30% (Gomberg and Buchler, *Chem. Rev.*, **1** (1925), 104), inspite of the presence of extremely negative anisyl radical.

(2) Montagne, *Rec. trav. chim.*, **27** (1908), 357.

charcoal. The ketone crystallised in slightly yellow scales with pearly lustre. A second recrystallisation from acetone gave practically colourless product melting at 136°C . which dissolves in concentrated sulphuric acid with orange colouration. The ketone is soluble in cold glacial acetic acid with an extreme difficulty, sparingly soluble in alcohol and ether, and readily soluble in benzene and hot acetone. The yield of the pure ketone amounted to about 40% of the theory.

Anal.: Subst. = 0.0784; CO_2 = 0.2566; H_2O = 0.0381 gr.

Found: C = 89.3; H = 5.45%.

Calc. for $\text{C}_{23}\text{H}_{16}\text{O}$ (Ketone): C = 89.6; H = 5.19%.

Reduction of the Ketone by Zinc Dust and Glacial Acetic Acid.

(a) *At High Temperature.* 3 Gr. of the ketone were reduced by 6 gr. of zinc dust and 12 c.c. of glacial acetic acid with boiling. When the reaction product was poured into a large quantity of water, slightly yellow crystalline cakes were produced and the aqueous solution turned a white emulsion. The cakes were drained on porous plate and purified from hot ligroin. As yellowish viscid substance separated first from the hot solution, the upper solution was decanted and cooled effectively. White crystals, grouped in burr-like shape were deposited on the side of beaker, which melted at 106°C . after a second recrystallisation from ligroin, and dissolved in concentrated sulphuric acid with beautiful violet colour similar to that of the methyl-violets solution. Further purification from the same solvent did not improve the product. However, when recrystallised from glacial acetic acid, the product melted at 111°C . and dissolved in concentrated sulphuric acid to colourless solution. It was determined to be β -naphthyl-diphenyl methane by elementary analysis and molecular weight determination. The yield of the pure compound was 30% of the theory.

Anal.: Subst. = 0.0706; CO_2 = 0.2418; H_2O = 0.0411 gr.

Found: C = 93.4; H = 6.68%.

Calc. for $\text{C}_{23}\text{H}_{18}$ (Naphthyl-diphenyl methane): C = 93.9; H = 6.12%.

Mol. weight, measured after Rast. Subst. = 0.139; Camphor = 2.06 mgr.;

M. p. depress. = 9.0°C . Found: mol. weight = 300.

Calc. for $\text{C}_{23}\text{H}_{18}$ (Methane): mol. weight = 294.

It was proved that the violet colouration produced by the product melting at 106°C ., when dissolved in concentrated sulphuric acid, was due to the corresponding carbinol contaminated as impurity, since the carbinol was formed by the reduction of the ketone with the same reagents but at room temperature, and it gave the same colouration when dissolved in concentrated sulphuric acid (See below).

(b) *At Room Temperature.* One gram of the ketone, dissolved in sufficient glacial acetic acid (ca. 300 c.c.) to keep it in solution at room temperature, was reacted with excess of zinc dust for four days. The filtrate from unchanged zinc dust was poured into water, and the resulting white precipitates were drained on porous plate and purified from ligroin. The product forms white crystalline powder which melts at 118°C. to colourless liquid. It was proved to be β -naphthyl-diphenyl carbinol from its composition and molecular weight. The yield was nearly quantitative.

Anal.: Subst. = 0.0636; CO_2 = 0.2065; H_2O = 0.0364 gr.

Found: C = 88.6; H = 6.41%.

Calc. for $\text{C}_{23}\text{H}_{18}\text{O}$ (Naphthyl-diphenyl carbinol): C = 89.0; H = 5.81%.

Mol. weight, measured after Rast. Subst. = 0.240; Camphor = 2.05 mgr.;

M. p. depress. = 14.5°C. Found: mol. weight = 323.

Calc. for $\text{C}_{23}\text{H}_{18}\text{O}$ (Carbinol): mol. weight = 310.

The carbinol is readily soluble in most organic solvents, but with great difficulty in cold ligroin. It dissolves in concentrated sulphuric acid with colouration of intense violet, similar to that of methyl-violets solution.

Sym. Di- β -Naphthyl-bis-Diphenyl Glycol,
$$\begin{array}{c} (\beta\text{-C}_{10}\text{H}_7)(\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4)\text{C}(\text{OH}) \\ | \\ (\beta\text{-C}_{10}\text{H}_7)(\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4)\text{C}(\text{OH}) \end{array}$$

Reduction of the Ketone by Magnesium and Magnesium Iodide. The reduction was carried out with 2 gr. iodine for magnesium iodide, 2 gr. of magnesium, 50 c.c. of ether-benzene and 2 gr. of β -naphthyl-diphenyl ketone, just in the same way as in the case of di-*p*-methoxy-benzophenone.⁽¹⁾ On shaking lightly yellowish-green solution, the colour changed red and heat was evolved, while magnesium was coated with brownish sticky substance. After an hour or more, magnesium was uncoated, an intense bluish-green solution being obtained, which changed greyish-green in colour, on further shaking. At this point the solution was hydrolysed. The pinacone, after digestion with hot alcohol to take off unchanged ketone and then with ether to remove coloured impurities, was recrystallised from benzene. The purified product weighed 1.3 gr. which was 65% of the theoretical yield. It begins to decompose at 156°C. and melted to a yellow liquid at 163°C., which, when remelted, begins to sinter at 90°C. and melts to a clear liquid at 123°C. The pinacone does not dissolve in concentrated sulphuric acid,

(1) This Bulletin, 7 (1932), 339.

while the sample, subjected to decomposition at melting point, dissolves in it with colouration of brownish-violet.

Anal.: Subst. = 0.0666; CO_2 = 0.2165; H_2O = 0.0356 gr.

Found: C = 88.6; H = 5.99%.

Calc. for $\text{C}_{46}\text{H}_{34}\text{O}_2$ (Pinacone): C = 89.3; H = 5.50%.

Rearrangement. 1.5 Gr. of this pinacone were boiled with the solution consisting of 20 c.c. of benzene, 10 c.c. of acetyl chloride, and 5 c.c. of acetic acid. The pinacone which was at first insoluble, gradually passed into solution with yellow colour, according as the rearrangement proceeded. After twelve hours' boiling the solvents were expelled under diminished pressure and the residue which formed yellow hard crusts was submitted to hydrolysis with 30 c.c. of 10% alcoholic potash. According with the progress of hydrolysis, white granular substance was observed depositing on the side of vessel. As the hydrolysis was found to require unexpectedly much of time, it was effected in two stages. After 48 hours' boiling, the alcoholic solution was decanted and the residue was extracted thrice with hot alcohol. The combined alcoholic solutions were analysed for organic acids, while the residue was boiled with a fresh addition of alcoholic potash for 240 hours.

Separation and identification of β -naphthoic acid and *p*-phenyl-benzoic acid in the presence of each other, were tried in various ways and were found to be hardly possible, though the individual acid has distinct properties (Table 2). Fortunately in the present case, these two acids appear in the different fractions of the hydrolysate, owing to a wide difference in facilities of scission of the two parent pinacolines.

Table 2.

	β -Naphthoic acid.	<i>p</i> -Phenyl-benzoic acid.
M. P.	182°C.	224°C.
Ag-salt.	Ag = 38.7%.	Ag = 35.4%.
Sublimate.	Feathery crystals.	Long silky fibres.
Thallo-salt.	Rosetted crystals.	Small diamond shaped crystals.
Ba-salt.	Needles with straight extinction, elongation negative.	Rhombs with diagonal extinction, elongation negative.

The acidic product in the first hydrolysate, when purified from ligroin with an addition of animal charcoal, crystallised in fine needles melting at 175°C., which was proved to be β -naphthoic acid contaminated with a minute quantity of *p*-phenyl-benzoic acid by the analysis of its silver salt. Microscopical examination of this product, however, failed to give the characteristic thallo-salt of β -naphthoic acid.

Anal.: Silver salt = 19.03; Ag = 7.41 mgr.

Found: Ag = 38.0%.

Calc. for silver naphthoate: Ag = 38.7%.

When this product was subjected to three successive crystallisations from ligroin, it melted at 182°C., sublimed in feathery crystals and gave the characteristic crystals of thallium- and barium salts under a microscope.

The acid obtained from the second hydrolysate, crystallised from ligroin in the forms of long white silky fibres, which melted at 224°C. and gave diamond shaped thallo-salt under microscope. Thereby, it was easily identified as *p*-phenyl-benzoic acid.

The yield of the crude β -naphthoic acid (m.p. 175°C.) amounted 0.04 gr. and that of *p*-phenyl-benzoic acid was nearly equal.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

A THEORY OF THE RATE OF SOLUTION OF GAS INTO LIQUID.
II. THE RATE OF SOLUTION OF GAS INTO LIQUID
CONTAINING A REACTING SUBSTANCE, AND
A KINETIC DERIVATION OF THE
DISTRIBUTION LAW.

By SUSUMU MIYAMOTO.

Received November 4th, 1932. Published December 28th, 1932.

Introduction.

For the rate of solution of gas into liquid the following expression was proposed by the present writer.⁽¹⁾

(1) S. Miyamoto, this Bulletin, **7** (1932), 8; *Journal of Science of the Hiroshima University*, A, **2** (1932), 73; *Chem. News*, **144** (1932), 273.

$$\frac{dn}{dt} = \frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} - \frac{c_l}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}} \dots (1)$$

where p is the partial pressure of the gas, M the molecular weight of the gas, R the gas constant, T absolute temperature, S the area of the boundary surface, c_l the concentration of the gas in the liquid phase expressed by moles/liter, n the number of moles of the gas in the liquid phase, and t the time.

The derivation of the above equation is based upon two assumptions, (a) that among the molecules of gas which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_0 , can enter into the liquid phase, and (b) that among the molecules of gas in the liquid phase, only those, which collide with the boundary surface with velocities, whose components at right angles to the boundary surface are greater than a threshold value u_0' , can escape from the liquid phase.

When the liquid is saturated with the gas,

$$\frac{dn}{dt} = 0.$$

Then in the state of saturation,

$$\frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} = \frac{c_\infty}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \dots (2)$$

where c_∞ is the concentration of the saturated solution.

From equations (2) and (1) we have,

$$\frac{dn}{dt} = \frac{c_\infty}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}} - \frac{c_l}{1000} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \dots (3)$$

or

$$\frac{dn}{dt} = KS(c_\infty - c_l), \dots (4)$$

where

$$K = \frac{1}{1000} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0'^2}{2RT}}, \dots (5)$$

Equation (4) is the well known equation, experimentally obtained and theoretically interpreted by the diffusion layer theory. When equation (4) is derived by the diffusion layer theory, the constant K is naturally conditioned by different factors from the constant involved in equation (5); the former is a function of the diffusion coefficient and the thickness of the supposed diffusion layer.

According to Brunner,⁽¹⁾ Davis and Crandall,⁽²⁾ the diffusion theory implies the existence of a stationary liquid film of a thickness of about 2×10^{-3} – 2×10^{-2} cm., the exact value naturally depending upon the rate of revolution of the stirrer in the main body of the liquid. When the liquid phase is well stirred, the question is whether a stationary liquid film of this thickness really exists at the interface. A direct confirmation is necessary.

It was proved by the present writer⁽³⁾ that the velocity of oxidation of sodium sulphite solution by oxygen in the presence of the molecular film of stearic acid or that of palmitic acid is almost identical with that in the absence of the molecules of these fatty acids. Now we must take into consideration from this experimental fact that when the main body of the liquid phase is well stirred, the thickness of the supposed stationary liquid film is smaller than the length of a molecule of the fatty acid⁽⁴⁾ employed (the length of the stearic acid molecule = 26.2×10^{-8} cm., and that of the palmitic acid molecule = 23.7×10^{-8} cm.). When the thickness of the stationary liquid film is as small as this, the mechanism of solution of gas can not be interpreted as a diffusion process.

The second assumption made in the diffusion layer theory is that the upper layer of the stationary liquid film is saturated instantaneously with the gas. If this assumption is correct, the rate of solution of gas should be considerable when the liquid phase is stirred so violently that new surfaces are constantly formed, but it has not yet been proved experimentally.

For the derivation of equation (4) from the theory of the present writer, neither the assumption of the existence of a stationary liquid film, nor that of the instantaneous saturation of the upper layer of the film with gas is necessary.

The Initial Rate of Solution of Gas into Liquid. The initial rate of solution of gas into liquid, or the rate of solution of gas when the liquid

(1) *Z. physik. Chem.*, **47** (1904), 99.

(2) *J. Am. Chem. Soc.*, **52** (1930), 3760.

(3) S. Miyamoto, T. Kaya and Nakata, this Bulletin **6** (1931), 133; *Journal of Science of the Hiroshima University, A*, **1** (1931), 203.

(4) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848; Adam, *Proc. Roy. Soc. London, A*, **99** (1921), 336; **101** (1922), 425, 516; **103** (1923), 676, 687.

is perfectly free from the gas, is expressed by the following equation, which is obtained by putting $c_l = 0$ in equation (4).

$$\left(\frac{dn}{dt}\right)_{\text{Initial}} = KS c_{\infty} \dots\dots\dots (6)$$

According to the diffusion layer theory, equation (6) gives the rate of diffusion of the gas molecules between the layer of concentration of saturation and that of zero.

According to the theory of the present writer the initial rate of solution of gas has a totally different character. From equations (6), (5) and (2) we have

$$\left(\frac{dn}{dt}\right)_{\text{Initial}} = \frac{p}{\sqrt{2\pi MRT}} S e^{-\frac{Mu_0^2}{2RT}} \dots\dots\dots (7)$$

This equation is directly obtained by putting $c_l = 0$ in equation (1). Equation (7) expresses the number of moles of gas which enter into the liquid phase per unit of time, when the liquid is perfectly free from gas molecules, the area of the boundary surface being S cm².

An important difference between the diffusion layer theory and the theory of the present writer is that the former assumes the instantaneous saturation of the upper layer of the liquid surface with gas, while the latter does not. According to the theory of the present writer the initial rate of solution of gas is expressed by equation (7), and a measurable time is necessary for the saturation of the upper layer of the liquid surface.

The Rate of Solution of Gas into Liquid Containing a Reacting Substance.

When the liquid contains a substance which reacts with the gas, the phenomenon is more complex. In the present paper only the initial rate of solution of gas, when the velocity of reaction between gas and reacting substance is considerable compared with the rate of solution, is discussed. Davis and Crandall⁽¹⁾ applied the diffusion layer theory in the following manner to the interpretation of the rate of solution of gas into liquid containing a reacting substance.

They assumed that the upper layer of the stationary liquid film is instantaneously saturated with the gas and that the gas molecules diffuse

(1) *J. Am. Chem. Soc.*, **52** (1930), 3769.

from this layer to the reaction zone, in which the concentrations of both gas and reacting substance remain at zero, and that the molecules of the reacting substance diffuse from the layer of concentration c_m to the reaction zone, c_m being the initial concentration of the reacting substance in the main body of the liquid phase.

They assumed that the initial rate of solution, experimentally observed, is no other than the rate of diffusion in this state, and derived the following equation for the initial rate of solution.

$$\frac{1}{S} \left(\frac{dn}{dt} \right)_{\text{Initial}} = k(c_{\infty} + c_m) . \quad \dots\dots\dots (8)$$

Equation (8) is inadequate for the complete interpretation of the experimental facts, as will be shown in what follows. It follows from equation (8) that the initial rate of solution increases consistently with the increase of concentration of the reacting substance c_m . At the same time the decrease of the initial rate of solution caused by the decrease of solubility of gas c_{∞} should be taken into account, as the solubility of gas c_{∞} decreases with the increase of the concentration of the reacting substance c_m . But c_{∞} generally has a small value. Therefore it is clear that when the value c_m is relatively great, the decrease of the value c_{∞} is negligible, and the initial rate of solution expressed by equation (8) should increase consistently as the value c_m is increased.

Contrary to what we should expect from equation (8), the initial rate of solution actually seems to decrease with the increase of concentration c_m when the value c_m is great. For example, the initial rate of solution of carbon dioxide into sodium hydroxide solution, observed by Ledig and Weaver,⁽¹⁾ increases with the increase of the value c_m when the value c_m is less than about 2.5 normal, and decreases when the value c_m is further increased.

The rate of solution of oxygen into sodium sulphite solution decreases with the increase of the concentration of sodium sulphite when the concentration is greater than about 1 normal.⁽²⁾ It is to be expected that the initial rate of solution of oxygen into concentrated sodium sulphite solution is less than that into dilute solution.

Equation (8) can not interpret these experimental facts.

This disaccord between equation (8), theoretically derived from the diffusion theory, and the experimentally observed facts would appear to

(1) *J. Am. Chem. Soc.*, **46** (1924), 650.

(2) S. Miyamoto and T. Kaya, this Bulletin, **6** (1931), 264; *Journal of Science of the Hiroshima University*, A, **2** (1932), 59.

be due to the assumption, employed for the derivation of equation (8), viz. that the upper layer of the liquid surface is instantaneously saturated with the gas.

The present writer is of the opinion that the initial rate of solution of gas in the presence of the reacting substance is expressed by equation (7) exactly as in the case of pure liquid. This does not mean that the presence of the reacting substance in the liquid phase has no effect upon the initial rate of solution of gas. As the value u_0 , in equation (7), is a constant depending upon the nature of the liquid phase, it varies with the change of concentration of the reacting substance in the liquid phase, and the initial rate of solution increases or decreases as the value u_0 decreases or increases.

Equation (7) does not contain a term c_∞ . This means that the initial rate of solution does not depend upon the solubility of gas. According to the theory of the present writer the solubility of gas is expressed as a function of $u_0'^2 - u_0'^2$ as will be seen in equation (9), while the initial rate of solution as a function of u_0 only.

The initial rate of solution of carbon dioxide into sodium hydroxide solution, observed by Ledig and Weaver,⁽¹⁾ is interpreted according to the new theory in the following way. At low concentrations the initial rate of solution increases with the increase of concentration of sodium hydroxide as the value u_0 decreases, and at high concentrations the initial rate of solution decreases with the increase of concentration of sodium hydroxide as the value u_0 increases.

In the case of the rate of solution of oxygen into sodium sulphite solution the value u_0 does not appear to be much effected by the increase of concentration of sodium sulphite at low concentrations, as the rate of solution of oxygen is independent of the concentration of sodium sulphite.⁽²⁾ The direct observation of the initial rate of solution of oxygen into sodium sulphite solution will be carried out on a later occasion.

A collaborator of the present writer is now studying the rate of solution of oxygen into alcoholic solution of anhydrous stannous chloride, and it has proved that the initial rate of solution is not much effected by the increase of concentration of stannous chloride at low concentrations, while the initial rate of solution decreases as the concentration of stannous chloride increases at high concentrations.⁽³⁾ This phenomenon is to be interpreted exactly as in the case of sodium sulphite solution.

(1) Loc. cit.

(2) Loc. cit.

(3) The result of this experiment will be published shortly.

The Solubility of Gas. From equation (2) we have,

$$c_{\infty} = \frac{1000}{RT} p e^{-\frac{M}{2RT}(u_0^2 - u_0'^2)} \dots\dots\dots (9)$$

The solubility of gas c_{∞} moles/liter is given by equation (9) according to the present theory. The solubility is not a function of u_0 only, but that of $u_0^2 - u_0'^2$.

The Calculation of u_0 and u_0' . From equation (7) we can calculate the value u_0 , if the initial rate of solution of gas be determined, and when the value of u_0 and the solubility c_{∞} are known, the value of u_0' is calculated from equation (9). In the case of oxygen and water the value of u_0 is⁽¹⁾

$$u_0 = 1.65 \times 10^5 \text{ cm./sec. at } 15^\circ\text{C.,}$$

and the solubility of oxygen at 15°C. is

$$c_{\infty} = 1.50 \times 10^{-3} \text{ moles/liter.}$$

The calculated value of u_0' from equation (9), using these values, is

$$u_0' = 1.49 \times 10^5 \text{ cm./sec.}$$

This means that among the molecules of oxygen in water, only those which collide with the interface with velocities whose components at right angles to the boundary surface are greater than a threshold value $1.49 \times 10^5 \text{ cm./sec.}$, are able to escape from the liquid phase.

A Kinetic Derivation of the Distribution Law.

In equation (9) c_{∞} is expressed by the number of moles per liter. If c_{∞} be expressed by the number of moles per c.c., equation (9) becomes

$$c_{\infty} = \frac{p}{RT} e^{-\frac{M}{2RT}(u_0^2 - u_0'^2)} \dots\dots\dots (10)$$

Equation (10) expresses the relation between the solubility and the partial pressure of gas. At constant temperature, the value $u_0^2 - u_0'^2$ can be considered to be constant, and then we have from equation (10)

$$c_{\infty} = k p, \dots\dots\dots (11)$$

where

$$k = \frac{1}{RT} e^{-\frac{M}{2RT}(u_0^2 - u_0'^2)} \dots\dots\dots (12)$$

(1) S. Miyamoto and A. Nakata, this Bulletin, **6** (1931), 21; *Journal of Science of the Hiroshima University, A*, **1** (1931), 143.

Equation (11) is Henry's law, and the constant k , according to the present theory, has the value given by equation (12). Now,

$$\frac{p}{RT} = \frac{1}{v} = c_g, \quad \dots\dots\dots (13)$$

where c_g is the concentration of gas in the gas phase. From equations (10) and (13) we have

$$\frac{c_\infty}{c_g} = e^{-\frac{M}{2RT}(u_0^2 - u_0'^2)}, \quad \dots\dots\dots (14)$$

or

$$\ln \frac{c_\infty}{c_g} = \frac{\frac{Mu_0'^2}{2} - \frac{Mu_0^2}{2}}{RT}. \quad \dots\dots\dots (14')$$

If the values of E_{x_0} and E_{x_0}' are given by

$$\frac{Mu_0^2}{2} = E_{x_0}, \quad \frac{Mu_0'^2}{2} = E_{x_0}', \quad \dots\dots\dots (15)$$

we obtain by substituting these values in equation (14),

$$\ln \frac{c_\infty}{c_g} = \frac{E_{x_0}' - E_{x_0}}{RT}. \quad \dots\dots\dots (16)$$

Equations (14) and (16) also give Henry's law.

The distribution of a substance between two liquid phases can be treated in exactly the same way. Consider a case in which a substance is distributed between two liquid phases A and B in one and the same molecular state. Then the rate of increase of the substance in phase B is expressed by

$$\frac{N}{S} \frac{dn}{dt} = N_1 - N_2 \quad \dots\dots\dots (17)$$

where N is Avogadro's number, N_1 the number of molecules which transfer through unit area of the boundary surface from phase A to phase B per second, N_2 the number of molecules which transfer through unit area of the interface from phase B to phase A per second, S the area of the boundary surface, n the number of moles of the substance in phase B, and t the time.

Now the following assumptions are proposed.

(a) Among the molecules of the distributed substance in phase A, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_1 , are able to enter into phase B, and

(b) Among the molecules of the substance in phase B, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_2 , are able to enter into phase A.

By Maxwell's distribution law, among N molecules, the number of molecules, whose components of velocities at right angles to a fixed plane lie between u and $u+du$, is expressed by

$$dN = \frac{N}{\sqrt{\frac{2\pi RT}{M}}} e^{-\frac{Mu^2}{2RT}} du.$$

Then it is clear that N_1 is expressed by the following equation.

$$N_1 = \int_{u_1}^{\infty} \frac{c_1 N}{\sqrt{\frac{2\pi RT}{M}}} u e^{-\frac{Mu^2}{2RT}} du = c_1 N \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_1^2}{2RT}}, \dots (18)$$

where c_1 is the concentration of the substance in phase A, expressed by moles per c.c. Similarly N_2 is expressed by

$$N_2 = \int_{u_2}^{\infty} \frac{c_2 N}{\sqrt{\frac{2\pi RT}{M}}} u e^{-\frac{Mu^2}{2RT}} du = c_2 N \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_2^2}{2RT}}, \dots (19)$$

where c_2 is the concentration of the substance in phase B expressed by moles per c.c. From equations (17), (18) and (19) we obtain

$$\begin{aligned} \frac{dn}{dt} &= c_1 S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_1^2}{2RT}} - c_2 S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_2^2}{2RT}} \\ &= S \sqrt{\frac{RT}{2\pi M}} \left(c_1 e^{-\frac{Mu_1^2}{2RT}} - c_2 e^{-\frac{Mu_2^2}{2RT}} \right). \dots\dots\dots (20) \end{aligned}$$

In the state of equilibrium

$$\text{and} \quad \left. \begin{aligned} c_1 &= c_{1\infty}, & c_2 &= c_{2\infty}, \\ \frac{dn}{dt} &= 0 \end{aligned} \right\} \dots\dots\dots (21)$$

From equations (20) and (21) we obtain

$$c_{1\infty} e^{-\frac{Mu_1^2}{2RT}} - c_{2\infty} e^{-\frac{Mu_2^2}{2RT}} = 0, \dots\dots\dots (22)$$

or

$$\frac{c_{1\infty}}{c_{2\infty}} = e^{\frac{1}{RT} \left(\frac{Mu_1^2}{2} - \frac{Mu_2^2}{2} \right)} \dots\dots\dots (23)$$

If $E_{x,1}$ and $E_{x,2}$ are expressed by

$$E_{x,1} = \frac{Mu_1^2}{2}, \quad E_{x,2} = \frac{Mu_2^2}{2}, \dots\dots\dots (24)$$

we obtain by substituting these values in equation (23)

$$\frac{c_{1\infty}}{c_{2\infty}} = e^{\frac{1}{RT}(E_{x,1} - E_{x,2})} \dots\dots\dots (25)$$

or

$$\ln \frac{c_{1\infty}}{c_{2\infty}} = \frac{1}{RT}(E_{x,1} - E_{x,2}) \dots\dots\dots (26)$$

When the temperature is constant, the values of u_1 and u_2 or those of $E_{x,1}$ and $E_{x,2}$ are constant and we have

$$\frac{c_{1\infty}}{c_{2\infty}} = \text{const.}$$

Equations (23), (25) and (26) give the distribution law derived according to the present theory.

The distribution law is usually derived thermodynamically by making the chemical potentials of the distributed substance in the two liquid phases equal in the state of equilibrium.⁽¹⁾ The chemical potentials μ_1 and μ_2 are expressed by

$$\left. \begin{aligned} \mu_1 &= K_1 + RT \ln x, \\ \mu_2 &= K_2 + RT \ln y, \end{aligned} \right\} \dots\dots\dots (27)$$

(1) R. Lorenz, *Z. anorg. allgem. Chem.*, **178** (1929), 346.

where x and y are the mole fractions of the substance in the two phases respectively. At equilibrium

$$\mu_1 = \mu_2$$

and we have

$$\ln \frac{x}{y} = \frac{1}{RT}(K_2 - K_1) \dots\dots\dots (28)$$

It is an interesting fact that equation (26), derived kinetically, has a form analogous with equation (28), obtained thermodynamically.

Summary.

(1) The initial rate of solution of gas into liquid was developed from a new theory of the rate of solution based upon the assumptions. (a) that among the molecules of gas, which collide with the interface, only those, whose components of velocities at right angles to the interface are greater than a threshold value u_o , can enter into the liquid phase, and (b) that among the molecules of gas in the liquid phase, only those, which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value u_o' can escape from the liquid phase.

The equations derived from the new theory were compared with those obtained from the diffusion layer theory.

(2) The solubility of gas was expressed as a function of u_o and u_o' .

(3) The values of u_o and u_o' were calculated in the case of oxygen and water at 15°C.

(4) Henry's law was derived by means of the new theory.

(5) The distribution of a substance between two liquid phases was discussed in exactly the same manner.

Laboratory of Physical Chemistry, Hiroshima University,
Hiroshima.