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ÜBER DIE SULFONIERUNG DES ROHRZUCKERS.

Von Tokuro SODA.

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Die Untersuchungen über Rohrzucker-schwefelsäure sind bis jetzt nur gering. Vielleicht könnte meine frühere Veröffentlichung⁽¹⁾ über diese Verbindung die letzte sein. Ihre Darstellung wurde durch direkte Sulfonierung des Rohrzuckers in Pyridin mit Chlorsulfonsäure ausgeführt und ihr Ba-salz hatte der Analyse nach die Zusammensetzung von Rohrzucker-mono-schwefelsäure (RS_I): $(C_{12}H_{21}O_{11}SO_3)_2Ba + 2C_2H_6O$. Das Salz war weisses amorphes Pulver; es wurde von Invertase zerlegt und durch Hefe vergoren; seine Einheitlichkeit ist doch noch nicht bewiesen. Da Hexose-schwefelsäure nicht durch Hefe in Gärung versetzt werden scheint, müsste der sulfonierte Hexose-Anteil der Rohrzucker-mono-schwefelsäure in der Gärgut zurückbleiben und daraus als Glucose- oder Fructose-mono-schwefelsäure erfassen lassen.

In vorliegenden Versuche wurde die Sulfonierung wie üblich in demselben Sulfonierungsapparat wie in der früheren Mitteilung⁽²⁾ geschildert ausgeführt: 20 gr. gut getrockneter fein gepulverter Rohrzucker wird in 70 ccm Pyridin durch heftiges Turbinieren suspendiert. Vom Tropftrichter wird ein Gemisch von 4 ccm Chlorsulfonsäure und 12 ccm Chloroform langsam eingetropft (das molekulare Verhältnis des Rohrzuckers zu Chlorsulfonsäure (R:S) wird etwas grösser als 1 gewählt). Das Gemisch lässt sich am Anfang auch unter Eiskühlung glatt umrühren, aber wenn etwa ein Drittel der Flüssigkeit zugesetzt ist, wird der ausgeschiedene Sirup plötzlich so zäh dass man die Temperatur bis auf 35–40°C. steigen lassen muss um weiter zu turbinieren.

So wird die weitere Sulfonierung in diesem Temperaturbereich durchgeführt. In der früheren Mitteilung wurde angegeben dass die Sulfonierung unter Kühlung ausgeführt war, jedoch meinte man damit nur im Anfang der Reaktion. Die Temperatur musste im Verlauf der Reaktion wesentlich erhöht werden um die Turbinierung weiter durchzuführen. Nach Beendigung des Eintropfens turbiniert man weiter einige Stunden bei Zimmertemperatur. Am nächsten Tag wird der zähe Sirup, der sich auf dem Boden abgesetzt hat, von oberen Pyridinschicht abgetrennt, in wasserfreiem Metanol aufgelöst und vom unlöslichen Rohrzucker (6–8 gr.) abfiltriert. Das Filtrat wird mit wenig Wasser ins Destillierkolben eingetragen und nach dem Austreiben des Metanols unter Zusatz von PbO abdestilliert bis es pyridinfrei wird. Weiteres Verfahren ist fast dasselbe wie bei Glucose-schwefelsäure⁽²⁾ angegeben ist.

Versuch I. In die Lösung des Pb-salzes von RS (Rohrzucker-schwefelsäure) wurde H₂S durchgeleitet und in die freie Säure umgewandelt. Die

(1) *Biochem. Z.* **135** (1923), 621.

(2) (1) und dieses Bulletin, **8** (1933), 37.

Disaccharid-schwefelsäure wurde im sauren Medium von selbst in Hexose-schwefelsäure gespalten. Nach Aufbewahren einiger Monaten im kühlen Ort, neutralisierte man die Lösung mit KOH und versetzte sie in Gärung. Nach Beendigung der Gärung wurde die Lösung von Hefe befreit, im Vakuum eingengt und das K-salz wurde aus Alkohol gefällt.

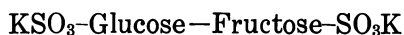
Die Analyse der vorgetrockneten Substanz* zeigte :

	S	K	$[\alpha]_D$
Gefunden	11.30%	13.25%	+26.5° (keine Mutarotation)
Ber. für $C_6H_{11}O_6SO_3K$	10.79	13.11	

Diese Analysenwerte stimmen ziemlich gut überein mit K-Hexose-mono-schwefelsäure, doch seiner optischen Drehung nach, ist es ganz verschieden von K-Glucose-6-mono-schwefelsäure ($[\alpha]_D = +37.3^\circ$). Alle Farbenreaktionen von Fructose (Proben von Seliwanoff, Ekkert, Dische⁽³⁾ und HCl) sind sehr deutlich. Könnte es also hier um K-Fructose-monoschwefelsäure handeln? Diese Vermutung scheint doch unzutreffend wenn man seine Reduktionsvermögen revidiert.

Reduktionsvermögen (als Glucose berechnet)		
	Substanz in Frage	K-Glucose-mono-6-schwefelsäure
gemessen	36 mg in 125 mg Subst.	28.8 mg in 48.3 mg Subst.
nach Bertrand	(28.7%)	(43.0%)
nach Willstätter-Schudel	8 mg in 37.7 mg Subst.	39 mg in 86.3 mg Subst.
	(21.2%)	(45.2%)

Aus diesem Resultat sieht man ein dass in K-Glucose-schwefelsäure, gemessen nach beiden Methodik, der Glucosegehalt praktisch gleich ist, während man bei der aus Rohrzucker dargestellten Substanz deutlich verschiedene Werte erhält. Ausserdem steht der Glucose-Gehalt in K-Glucose-schwefelsäure ungefähr 2 Mal so hoch als in der Substanz in Frage wenn sie nach Willstätter-Schudel gemessen wird. Es scheint also als ob die Hälfte von der Substanz aus Glucose-6-mono-schwefelsäure bestehe. Aus obigen Versuche liegt die Annahme nahe dass das Sulfonierungsprodukt von Rohrzucker wesentlich die folgende chemische Substanz sei :



Nach dieser Auffassung könnte mein früheres Ba-salz von RS_1 ein zufälliges Gemisch oder eine lockere Assoziationsverbindung von $RS_2Ba + R$ gewesen sein. Tatsächlich, bei vielen Sulfonierungsexperimenten schwankte der

* Die Trocknung wird gewöhnlich bei 80°C. im Vakuum ausgeführt. Bei 100°C. nimmt das Gewicht weiter ab, aber schliesslich tritt gelbe Färbung ein. Die so lange erhitzte Substanz zeigte ein interessantes Verhalten zum Wasser: beim Lösen in Wasser entwickelte sie CO_2 ; die Lösung war fast neutral (pH: ca 6) und reduzierte Fehlingsche Lösung in der Kälte; Spaltung der organisch gebundenen SO_4 war nur gering.

(3) *Chem. Abstr.*, **23** (1929), 4766.

Ba-Gehalt von Rohprodukten zwischen 10 und 16%. Man könnte dann vermuten dass sulfonierter Anteil sich nicht von Hefe vergären lässt: es ist also der assoziierte R der durch Invertase zerlegt wird.

Versuch II. Rohes Ba-salz von Rohrzucker-schwefelsäure (RS-Ba I) dessen Ba-Gehalt 15.9% betrug, wurde durch Brucinsulfat versetzt. Das erhaltene Brucin-salz (RS-Brc I) welches sich nicht ohne weiteres kristallisieren liess, wurde aus Alkohol als amorphes Pulver gefällt. Es enthielt 5.06% S und zeigte $[\alpha]_D = -1.63^\circ$. S-% berechnet aus $C_{12}H_{20}O_{11}(SO_3HC_{23}H_{25}O_4N_2)_2 = 4.95\%$. Aus diesem Brucin-salz wurde das Ba-salz wieder hergestellt. Sein S- und Ba-Gehalt waren:

	S	Ba
Gefunden	10.80%	23.14%
Ber. für RS_2 -Ba	10.03	21.54
Ber. für RS_3 -Ba	11.52	24.62

Ferner wurde dieses Ba-salz wieder ins K-salz umgewandelt: sein S-Gehalt = 11.30%. (Ber. für RS_2 -K = 11.09%); $[\alpha]_D = +47^\circ$.

Durch Invertase trat nur geringes Reduktionsvermögen auf, während durch Säure es stark zunahm. Am Ende der Säure-spaltung sank seine $[\alpha]_D$ auf $+27.1^\circ$ ab. Nach längerem Aufbewahren seiner wässrigen Lösung schieden sich eigentümliche spiral-förmige Kristalle aus. (Abb. 1).



Abb. 1.

Versuch III. Solche spirale Kriställchen von Brucin-salz wurden auch aus dem Ba-salz (RS-Ba XVII) erhalten. Sein Ba-Gehalt war 13.6%. Daraus bereitetes Brucin-salz wurde in heissem Pyridin gelöst und allmählich Alkohol zugesetzt. Beim Erkalten setzte sich auf dem Boden ein Sirup ab, welcher von Mutterlauge getrennt, mit Alkohol zerrieben wurde. Das weisse Pulver wurde abgesaugt und mit Alkohol gut gewaschen und getrocknet. Sein S-Gehalt = 4.76%, 4.77%. Aus seiner wässrigen Lösung schied sich spirale Kristalle aus (ihr optischer Charakter: negativ) (Abb.

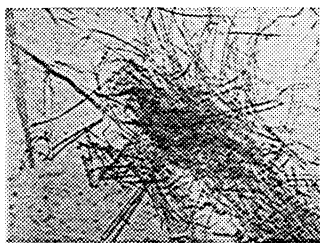


Abb. 2.

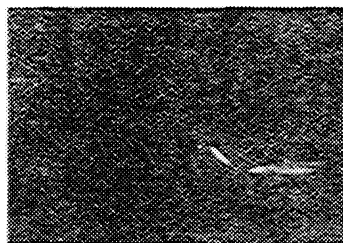


Abb. 3.

2 und 3). S-Gehalt = 5.71% (ber. für RS₄-BrC = 5.73%), $[\alpha]_D = -9.64^\circ$. Ausbeute 0.6 gr. aus 15 gr. Ba-salz.

Versuch IV. Die rohen Präparate von Ba-salze (RS-Ba XXIV, XXV, XXVII) deren Ba-Gehalt zwischen 10 und 13% liegen, wurden durch Hefe vergoren. Ausgegorene Flüssigkeit wurde von der Hefe abfiltriert, eingengt und aus Alkohol gefällt. Ihr Ba-Gehalt stieg auf: 18.34% für RS-Ba XXIV, 19.84% für RS-Ba XXV und 18.03% für RS-Ba XXVII. Beim Anfang der Gärung zeigte die Flüssigkeit sehr starke Reduktion, aber die durch Hefe gereinigten Ba-salze enthielten nur Spur von reduzierende Substanz, und erst nach der Behandlung durch Säure trat starke Reduktion heraus. Unten wird die Zunahme der Reduktion beim Erhitzen einer Lösung von RS-Ba XXV mit 0.02 N HCl auf 100°C gezeigt. Das Reduktionsvermögen wird nach Hagedorn-Jensen-Hanessche⁽⁴⁾ Methode gemessen und als % von Glucose des gelösten Ba-salzes dargestellt.

5 ccm der 1.673%-ige Lösung vom Ba-salz enthielten nach dem Reduktionsvermögen 2.64 mg Glucose; daher 52.8 mg Glucose in 1.673 gr. der Substanz oder 3.08% (die chemische Eigenschaft dieser kleinen Menge der reduzierenden Substanz ist noch nicht untersucht). Nun wurde zu anderen 5 ccm der Lösung 1 ccm HCl (0.53 N) zugefügt, auf 25 ccm verdünnt und im siedenden Wasserbad eingetaucht. Von Zeit zu Zeit pipettierte man daraus 2 ccm und neutralisierte es mit 0.4 ccm NaOH (0.112 N). Dieses wurde mit Wasser auf 5 ccm verdünnt und analysiert. Wenn es z.B. A mg Glucose ergibt, so berechnet man Glucose-Menge in 1.673 gr. der Substanz (B mg) : $A \times 25/2 \times 100/5$. Glucose-% = B/16.73.

Min.	A	B	Glucose-%	Zunahme der Reduktion
0	—	52.8 mg	3.1	0
10	1.75	437	26.1	23.0
15	2.01	502	30.0	26.9
30	2.21	552	33.0	29.9
45	2.26	570	34.1	31.0
90	2.32	580	34.7	31.6
120	2.34	585	35.0	31.9

Nach 120 Min. wurde die Lösung ein wenig gelblich und eine schwache Trübung von BaSO₄ trat ein. Dieselbe Lösung, gemessen nach Willstätter-Schudel, zeigte ein Reduktionsvermögen 20.8% Glucose oder 22.9% umgerechnet für K-salz welcher Wert mit dem vorher angegebenen 21.2% (Versuch I) ziemlich gut übereinstimmt. $[\alpha]_D$ zeigte anfangs +37° und nach der Hydrolyse +26°. Daher ist die vorangehende Annahme festgestellt dass RS₂ nicht durch Hefe aufgespalten sondern erst durch Säure in Glucose- und Fructose-schwefelsäure hydrolysiert wird.

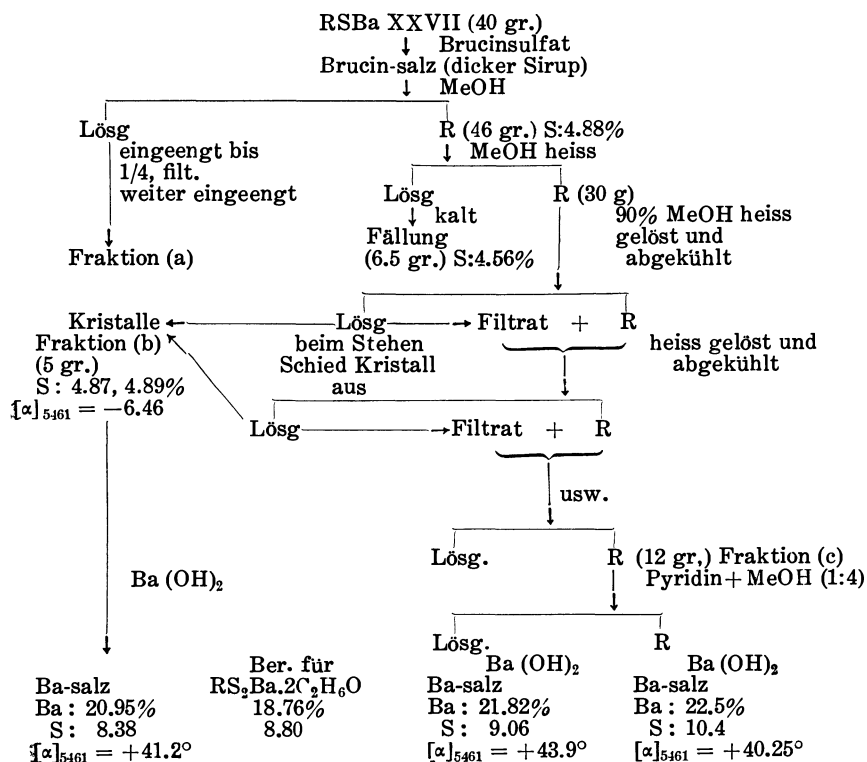
Versuch V. RS₂ muss dem Analysenwert nach das Hauptprodukt der Sulfonierung sein. Um RS₂ zu isolieren wurde Brucin-salz aus RS-Ba XXIV

(4) *Biochem. J.*, **23** (1929), 99.

dargestellt. Zum dick konzentrierten Sirup wurde Metanol zugefügt bis Fällung gerade eintrat und dieses im Eisschrank aufbewahrt. Zu erst schieden sich radial kugelförmige Kristalle aus und später erstarrte das Ganze in einem Kristall-brei. Das einzelne Kristall ist ein feines Nadelchen und positiv in optischen Charakter. Nach zweimaligem Umkristallisieren wurde es analysiert: sein S-Gehalt war 5.19% oder 5.14%. Dieser Analysenwert ist ein wenig grösser als der S-Gehalt von RS_2 -Bruc (4.95%) doch viel kleiner als RS_3 -Bruc (5.45%). Der Berechnung nach erhalten wir diesen Wert als solches Gemisch wie $2RS_2 + RS_3$ oder $5RS_2 + RS_4$.

Versuch VI. Das Brucin-salz aus $RSBa$ XXV kristallisierte aus seiner sirupösen wässrigen Lösung in nadelförmigen Kristalle. Kristallisierte man es aus Metanol um, so schied sich haardünne Kristalle (opt. Charakter positiv) aus. Es wurde mit kaltem Wasser einige Mal gewaschen und getrocknet. Die Ausbeute war sehr gering. Sein S-Gehalt war: 5.35% was sehr nahe dem S-Gehalt von RS_3 -Bruc. steht.

Versuch VII. Fast reines Brucin-salz von RS_2 wurde aus $RSBa$ XXVII mit 90%-igem Metanol erhalten, zwar in folgendem Schema:



Fraktion (a): eine braune zähe Masse, die schwer weiter zu reinigen ist. RS_1 könnte hier vorhanden sein wenn es überhaupt existiert. Fraktion (b): Kristalle von RS_2 -BrC—beim Abdampfen seiner wässrigen Lösung schieden sich ganz homogene schöne Kriställchen aus; sein optischer Charakter ist sonderbar: eine optische Achse liegt nicht parallel mit der Entwicklungsrichtung des Kristalles. (Abb. 4 u.

5). Fraktion (c): erstarrte in eine feste amorphe Masse wenn sie gut trocknen liess. Beim Aufbewahren um mehrere Monate in kühlem Ort schied sich feine Kriställchen aus, aber diese Kristalle sind in glasige amorphe Masse eingebettet; deshalb ist diese Fraktion unrein. Nach der Behandlung mit Pyridin + MeOH

wurde es ins Ba-salz umgesetzt. Seinem Ba- und S-Gehalt nach ist es wohl ein Gemisch von RS_2 und RS_3 oder noch höheren Ester zu betrachten. In die Waschflüssigkeit ging die Hauptmenge von RS_2 über. Merkwürdig ist es dass alle Ba-salze, die über Brucin-salz dargestellt sind, mehr Ba enthalten als die entsprechende S verlangt. Es ist wohl denkbar dass Rohrzuckerschweifelsäure bei der Behandlung mit überschüssigem Baryt, mit diesem saccharatartig verbinden könne⁽⁵⁾.

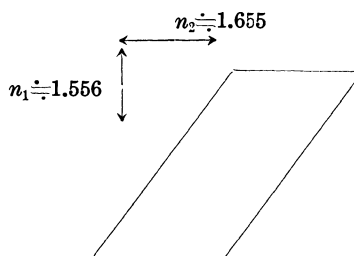


Abb. 4.

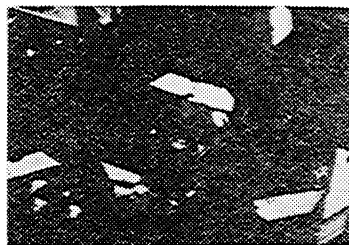
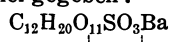


Abb. 5.

Versuch VIII. Nun wurde die Sulfonierungsbedingung so abgeändert dass das molekulare Verhältnis von Rohrzucker (20 gr.) zur Chlorsulfonsäure $R:S = 1:2$ wird. Nach dem Austreiben des Pyridins durch PbO , bildete ein Teil des sulfonierten R eine unlösliche Verbindung mit PbO (A) und der Restanteil ging als Pb-salz in das Filtrat über (B) (RS -Ba XXII). Aus (A)

(5) Eine dergleichen Deutung findet man in der Mitteilung von Neuberg und Pollak (*Ber.* **43** (1910), 2060). Sie haben zu ihrem Ba-salz der Rohrzuckerschweifelsäure folgende chemische Formel gegeben:



erhielt man 4 gr. Ba-salz (Ba : 22.18%) und aus (B), 22 gr. Ba-salz (Ba : 13.81%). Das letztere, nach der Vergärung durch Hefe, liess seinen Ba-Gehalt bis 18.03% steigen (nach dem Trocknen bei 80°C. im Vakuum 20.0%). Ausbeute : 6 gr. aus 10 gr.

Brucin-salz aus RS-Ba XXII (A) ist im Wasser wenig löslich und lässt sich aus heissem Wasser umkristallisieren. Das Kristall ist optisch negativ und etwas spiralförmig; S-Gehalt = 5.62, 5.63%. Brucin-salz aus RS-Ba XXII (B) ist im Wasser leicht löslich. Aus dem Sirup schied sich nur eine kleine Menge von nadelförmige Kristalle (optisch positiv) aus; sein S-Gehalt = 5.36%.

Versuch IX. Schliesslich wurde das molekulare Verhältnis R:S bei der Sulfonierung bis 1:3 erniedrigt. Alle organisch gebundene Schwefelsäure vereinigten mit unlöslichem PbO. Es wurde durch H_2S zersetzt und ins Ba-salz übergeführt. Das Ba-salz enthielt 25.7% Ba. Das daraus hergestellte Brucin-salz (S: 5.21%) enthielt reichliche Menge von spiralen Kristalle

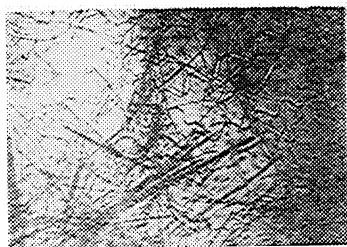


Abb. 6.

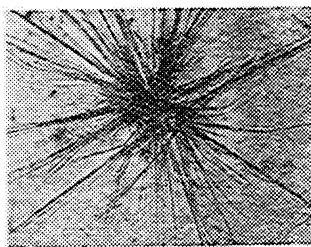


Abb. 7.

(Abb. 6 u. 7), und nach Umkristallisieren aus wässrigem Alkohol stieg sein S-Gehalt bis auf 5.86%. Aus der Mutterlauge ausgeschiedene Kristalle waren nach der Umkristallisation fein nadelförmig und sein S-Gehalt war 4.70%.

Schlussbemerkungen. Sulfonierung des Rohrzuckers verläuft also nicht so einfach wie bei Glucose. Wenn auch die Darstellung unter gleicher Sulfonierungsbedingung wie $R:S > 1$ durchgeführt wird, so ist das Reaktionsprodukt immer ein Gemisch von di-, tri- oder tetra-Ester, und zwar schwankt ihr Verhältnis von Ansatz zu Ansatz. Beim Sulfonieren unter starker Abkühlung wäre die Bildung des mono-Esters möglich, doch ist diese Bedingung praktisch kaum zu erfüllen.

Da Fructose, nach unseren Erfahrungen, auch unter schonender Bedingung leicht poly-Ester zu geben scheint (siehe dieses Bulletin 9, Nr. 2. "Glucosulfatase IX."), ist es anzunehmen dass der Fructose-Teil des Rohrzuckers auch geneigt sei poly-Ester zu bilden. Demnach ist mono-

Ester der Glucose in Rohrzuckerschweifelsäure zu erwarten, und zwar als Glucose-6-mono-schwefelsäure. Doch ist diese Gedankengang durch Experiment bis jetzt nicht völlig gestützt worden. Zuweilen habe ich sehr ähnliche Kristalle (auch der optische Charakter) wie Brucin-salz von

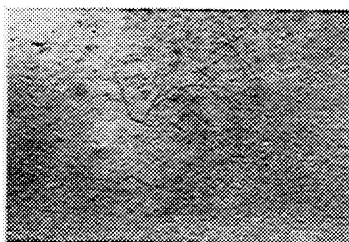


Photo. 8.

Glucose-6-mono-schwefelsäure in zerlegten Rohrzucker-schwefelsäure erkannt (Abb. 8), doch ist mir ihre Isolierung noch nicht gelungen. Das Verhalten gegen Gluco-sulfatase⁽⁶⁾ ist nennenswert: Die organisch gebundene SO_4 des durch Säure zerlegten $\text{RS}_2\text{-Ba}$ wird vom Enzym hydrolysiert, zwar ungefähr die Hälfte wie bei Glucose-6-mono-schwefelsäure; auf der durch Säure nicht zerlegten Rohrzucker-schwefelsäure wirkt das Enzym nur

schwach (demnächst veröffentlicht).⁽⁷⁾ Diese Tatsachen sprechen für die obige Vermutung, doch ist es schwer zu verstehen dass das K- oder Brucin-salz von zerlegten Rohrzucker-schwefelsäure keine Mutarotation zeigt.

Diese Arbeit wurde teilweise mit Mitteln von Kultusministerium zur Förderung der Wissenschaften ausgeführt, wofür ich zu grossem Dank verpflichtet bin.

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(6) dieses Bulletin, **6** (1931), 358; **8** (1933), 65; **8** (1933), 148.

(7) dieses Bulletin, **9**, Nr. 2. "Glucosulfatase IX."

OXIDATION OF SOME α -HYDROXY-ACIDS
WITH LEAD TETRA-ACETATE.⁽¹⁾

By Haruomi ÔEDA

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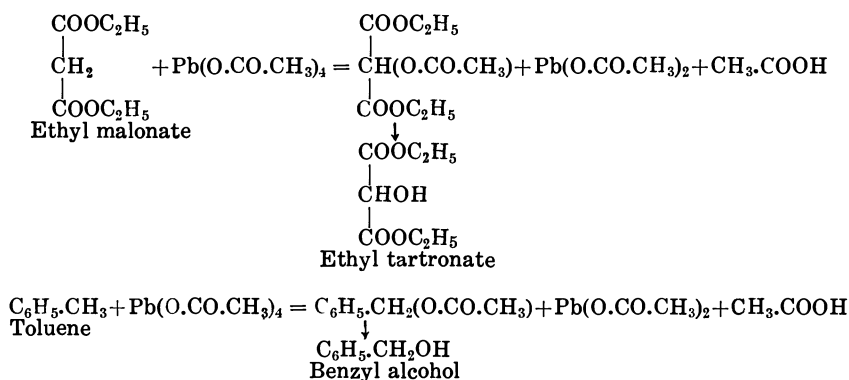
Lead tetra-acetate, the tetravalent lead salt of acetic acid, was introduced by Dimroth as a new oxidising agent. This salt is easily prepared from minium and acetic acid. It was recommended by him as a more convenient oxidising agent than lead peroxide itself in two respects. First, it is soluble in organic solvents such as benzene or glacial acetic acid, and the oxidation can be smoothly carried out as homogeneous reaction in these

(1) Studies on Hydroxy-acids and their Derivatives. Part I.

solvents. Secondly, after the oxidising action, it changes to lead acetate, which easily separates out as crystals when ether is added to the solution.

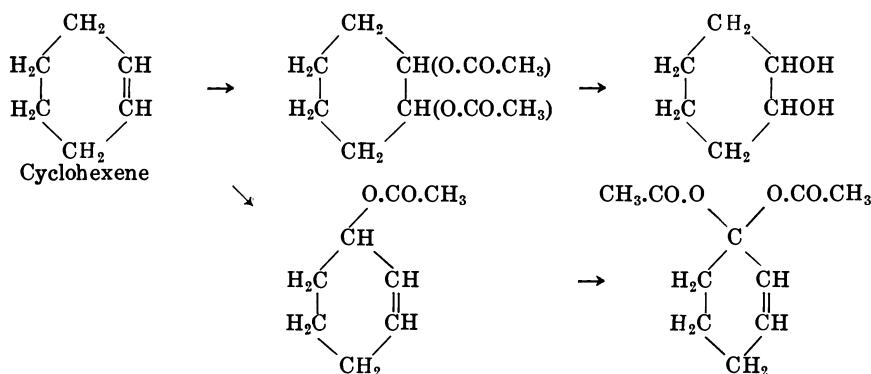
Various oxidation reactions hitherto described by Dimroth, Criegee and others are summarised as follows.

I.⁽²⁾ The reagent is efficient for the conversion of hydrogen atom into hydroxyl group, especially in the case of substances such as ethyl malonate, ethyl acetoacetate and acetone which contain labile hydrogen atoms ($-\text{CH}_2\text{CO}-$). It can also be applied to the homologues of toluene.



II.⁽³⁾ Oxidation of unsaturated substances of hydroaromatic type with this reagent occurs in two ways :

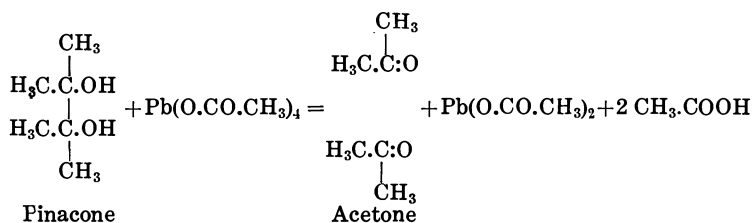
- (1) addition of two acetoxy-groups to the double linking, and
- (2) substitution of the adjacent hydrogen atoms by acetoxy-groups, whilst the double linking is unattacked.



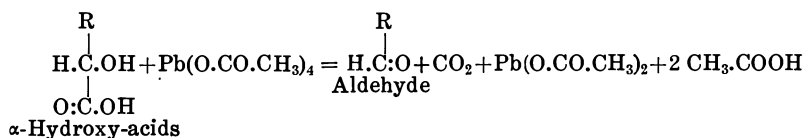
(2) O. Dimroth u. R. Schweizer, *Ber.*, **56** (1923), 1375.

(3) R. Criegee, *Ann.*, **481** (1930), 263.

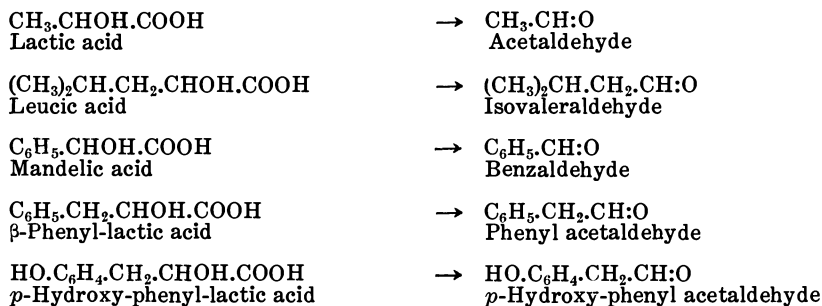
III.⁽⁴⁾ Glycols are oxidised by this reagent, yielding two molecules of carbonyl compounds.



Now, α -hydroxy-acids have analogous structure with glycols, namely, both of these compounds contain two hydroxyl groups combined to two neighbouring carbon atoms. Assuming that the oxidation of the same type occurs in the case of α -hydroxy-acids as in the case of glycols, the formation of aldehydes is easily expected.



The present author tried the oxidation of some simple α -hydroxy-acids with lead tetra-acetate and confirmed the formation of aldehyde from each of the following five acids.*



The oxidation of α -hydroxy-acids to aldehydes having an atom of carbon less is a reaction which can be performed with many oxidising agents. But

(4) R. Criegee, *Ber.*, **64** (1931), 260. H. Raudnitz u. J. Peschel, *Ber.*, **66** (1933), 903. The reagent was utilised for the differentiation between furanose and pyranose forms of sugars, since, on oxidation with this reagent, formaldehyde can result only when CH_2OH is adjacent to a free hydroxyl, namely, from the furanose modification. R. Criegee, *Ann.*, **495** (1932), 211.

* Japanese Patent : 98,241 (Suzuki, Takayama, Ôeda.)

at times the reactions produce not only expected aldehydes but also other oxidation products of further advanced stage. For example, when phenyl-lactic acid is oxidised with lead peroxide, it yields the mixture of benzaldehyde and phenyl acetaldehyde. In the case with lead tetra-acetate, there is no fear of such extreme oxidation, as this acts only as a dehydrogenating agent.

Experimental Part.

General. Lead tetra-acetate was prepared according to the description of Dimroth. Red lead oxide (minium) (400 gr.) was gradually added to glacial acetic acid (1000 gr.), which was thoroughly stirred and kept at 45–55°C. On cooling, a considerable amount of lead tetra-acetate was precipitated. It was obtained as colourless crystals on warming with a small bulk of warm acetic acid. Lead tetra-acetate is very hygroscopic and is, on exposure to moisture, easily decomposed to lead peroxide and acetic acid.

In each experiment, α -hydroxy-acid (10 gr.) was dissolved in benzene (120–150 c.c.) and an equimolecular amount of lead tetra-acetate was added to it. But, when the sample is not sufficiently soluble in benzene, glacial acetic acid was used as the solvent. Oxidation mixture was vigorously stirred throughout the whole operation.

During the course of the oxidation a small bulk of the solution was pipetted out from time to time and water was added to it. The completion of oxidation was roughly indicated by the termination of separation of lead peroxide.

Oxidation of Lactic Acid. Lactic acid (Merck) was subjected to vacuum distillation, when the main part distilled at 126–133°C. under 16 mm. The distillate (10 gr., 0.11 mol) was dissolved in warm glacial acetic acid (100 c.c.), and the solution was put in a flask having three necks, provided with a mechanical stirrer, an inlet for the oxidising agent and a reflux condenser to which two absorption bottles filled with cooled (–12°C.), dry ether were connected. The flask was kept at 50°C. on the water bath and lead tetra-acetate (44 gr., 0.11 mol) was added little by little. During the oxidation a rapid current of dry carbon dioxide was passed from the inlet tube through the whole apparatus. The aldehyde formed by the oxidation was completely absorbed by the ether.

After the completion of oxidation, dry ammonia was passed through the ether, and acetaldehyde was precipitated as aldehyde-ammonia. It melted at 88°C. and the yield was 3.0 gr. representing 45% of the hydroxy-acid used.

Identification of the Aldehyde. The aldehyde-ammonia was added to an aqueous solution containing roughly the equivalent amount of semicarbazide hydrochloride. On cooling, semicarbazone of acetaldehyde⁽⁵⁾ crystallised out, which melted at 160–162°C. after recrystallisation from water.

Anal. : Subst. = 2,249 mg., N = 0.832 c.c. (23.0°C., 762.4 mm.)

Found : N = 42.09%

Calc. for $C_3H_7ON_3$: N = 41.57%

Oxidation of Leucic Acid. *l*-Leucic acid was prepared by the action of nitrous acid upon natural leucine and it was precipitated as zinc salt. The free acid melted at 73°C. after recrystallisation from benzene.

Leucic acid (10 gr., 0.076 mol) was dissolved in benzene (140 c.c.). The solution was kept at 60°C. and lead tetra-acetate (33 gr., 0.76 mol) was added in the course of an hour. During the oxidation lead acetate separated out as a viscous jelly and then gradually changed to a crystalline mass. Benzene was decanted and the residue was well washed with a new bulk of benzene.

The combined benzene solution was shaken with an aqueous solution of sodium bicarbonate to remove acids. After drying, the solvent was removed by distilling on a boiling water-bath, simple still-head being provided. The greater part of benzene was distilled off without considerable loss of the aldehyde, though the complete separation was impossible. The residual oil was subjected to distillation, when the main part (4.9 gr.) distilled at 82–84°C., but it was not free from benzene.

Identification of the Aldehyde. *p*-Nitrophenyl hydrazine dissolved in five times of its weight of 40% aqueous acetic acid was added to the aqueous solution saturated with aldehyde. *p*-Nitro-phenyl hydrazone of isovaleraldehyde⁽⁶⁾ separated as flocculent precipitates. It melted at 109°C. after recrystallisation from alcohol.

Anal. : Subst. = 2.780 mg., N = 0.467 c.c. (26.0°C., 766.5 mm.)

Found : N = 19.33%

Calc. for $C_{11}H_{15}O_2N_3$: N = 19.00%

Oxidation of Mandelic Acid. *dl*-Mandelic acid (Merck, m.p. 118°C.) (10 gr., 0.066 mol) was dissolved in benzene (150 c.c.) and lead tetra-acetate (27 gr., 0.066 mol) was added. Further treatments were the same as described above. After removing benzene, the residual oil was distilled in vacuo. The part distilling at 72–73°C. under 21 mm. amounted to 3.7 gr. representing 54%.

(5) J. Thiele u. J. Bailey, *Ann.*, **303** (1898), 79.

(6) D. Dakin, *J. Biol. Chem.* **4** (1908), 236.

Identification of the Aldehyde. The aldehyde was added to an alcoholic solution of *p*-nitro-phenyl hydrazine. On cooling, *p*-nitro-phenyl hydrazone of benzaldehyde⁽⁷⁾ separated out. It melted at 189°C. after recrystallisation from alcohol with an addition of animal charcoal.

Anal. : Subst. = 2.973 mg., N = 0.466 c.c. (30.0°C., 759.4 mm.)

Found : N = 17.64%

Calc. for $C_{13}H_{11}O_2N_3$: N = 17.43%

Oxidation of Phenyl-lactic Acid. *l*-Phenyl-lactic acid was prepared by the action of nitrous acid upon natural phenyl alanine. It melted at 124°C. after recrystallisation from chloroform.

Phenyl-lactic acid (10 gr., 0.060 mol) was added to benzene (150 c.c.). The greater part of the acid can be brought into dissolution when the solution is kept boiling. Lead tetra-acetate (26 gr., 0.060 mol) was then added. Further treatments were the same as in the previous two cases.

After removing benzene, the residual oil was distilled in vacuo. The part distilling at 84–86°C. under 17 mm. amounted to 4.2 gr. representing 58%.

Identification of the Aldehyde. Alcoholic solutions of neutral hydroxylamine and of the aldehyde were mixed and allowed to stand overnight. A large volume of ether was then added and the excess of hydroxylamine was removed by extraction with water. Oxime of phenyl acetaldehyde thus prepared⁽⁸⁾ was soluble in hot petroleum ether, from which it can be recrystallised. It melted at 101–102°C.

Anal. : Subst. = 4.202 mg., N = 0.381 c.c. (24.0°C., 751.9 mm.)

Found : N = 10.31%

Calc. for C_8H_9ON : N = 10.36%

Oxidation with Lead Peroxide. Phenyl-lactic acid (5 gr.) was added to a mixture of water (20 c.c.) and phosphoric acid (5 c.c.). The presence of the latter prevented the formation of insoluble lead salt. Lead peroxide (13 gr.) was poured to the solution little by little, interrupting each time the steam which was passed into the flask throughout the reaction to transfer the aldehyde formed into the distillate.

The aldehyde (1.2 gr.) was obtained from the distillate after removing acidic part. About the half of hydroxy-acid was recovered from the residue.

The aldehyde obtained from several oxidations was brought together and subjected to vacuum distillation. It distilled at 65–80°C. under 22 mm.

(7) H. Biltz u. F. Sieden, *Ann.*, **324** (1902), 321.

(8) C. Harries u. A. de Osa, *Ber.*, **37** (1904), 843.

(lower than that of the oxidation product with lead tetra-acetate). The formation of crystalline oxime from the above sample was not successful. After long standing the colourless crystals were deposited from the distilled aldehyde and it amounted to 0.5 gr. It melted at 122°C. after recrystallisation from water, and showed no depression of melting point when mixed with a pure specimen of benzoic acid. The benzoic acid thus obtained may be regarded as an oxidation product of benzaldehyde in air. This fact shows that the aldehyde obtained was a mixture of benzaldehyde and phenyl acetaldehyde.

Oxidation of *p*-Hydroxy-phenyl-lactic Acid. *l-p*-Hydroxy-phenyl-lactic acid was prepared by the action of barium nitrite upon dilute sulphuric acid solution of natural tyrosine. It melted at 166°C. after recrystallisation from water.

p-Hydroxy-phenyl-lactic acid (2 gr., 0.011 mol) was dissolved in glacial acetic acid (60 c.c.) and the solution was kept at 50°C. Lead tetra-acetate (10 gr., 0.011 mol) was then added. The solution gradually assumed reddish tint. After cooling, a large volume of ether was added to precipitate the greater part of lead acetate. After complete separation of lead salt, ether was expelled under reduced pressure, and then the temperature was raised to 60°C. to remove the rest of acetic acid.

Identification of the Aldehyde. *p*-Hydroxy-phenyl acetaldehyde was obtained by Langheld⁽⁹⁾ when he oxidised tyrosine with sodium hypochlorite. No other information on this aldehyde was found in the literature.

To the residue of above distillation, an alcoholic solution of *p*-nitro-phenyl hydrazine (1:6) was added. On cooling, flocculent precipitates of reddish brown tint were formed, which were separated and moistened with a few drops of alcohol. It changed to crystalline mass taking one molecule of alcohol as alcohol of crystallisation. After recrystallisation from alcohol, it began to sinter at 165°C.

Anal. : Subst. = 1.806 mg., N = 0.210 c.c. (25.0°C., 761.5 mm.)

Found : N = 13.35%

Calc. for $C_{14}H_{13}O_3N_3 + C_2H_5OH$: N = 13.20%

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(9) K. Langheld, *Ber.*, **42** (1909), 2360.

ON THE ALKALOIDS OF WHITE HELLEBORE. I. ISOLATION OF CONSTITUENT ALKALOIDS.

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Since in 1819 Pelletier and Caventou⁽¹⁾ obtained from white hellebore, *Veratrum album* roots, a sternutatory alkaloidal body, which they called "veratria," Simon⁽²⁾, Will⁽³⁾, Tobien⁽⁴⁾ and other chemists and pharmacists have studied *Veratrum album* and other allied species (*V. viride*, *V. nigrum* etc.) with results in many respects contradictory of each other.

An important contribution to the knowledge of alkaloids of *Veratrum album* was made by Wright and Luff⁽⁵⁾, who treated the crushed dried roots with alcohol containing tartaric acid and showed that they contained at least five different alkaloids. Jervine, $C_{26}H_{37}NO_3$; pseudojervine, $C_{29}H_{43}NO_7$ and rubijervine, $C_{26}H_{43}NO_2$ were well-defined crystallisable nonsternutatory bases and a fourth, veratralbine, $C_{24}H_{43}NO_5$ was amorphous and nonsternutatory whilst the fifth, veratrine, $C_{27}H_{53}NO_{11}$ was highly sternutatory.

Seven years later Salzberger⁽⁶⁾ was able to isolate besides the above-mentioned three crystallisable bases, jervine, pseudojervine and rubijervine, two new minor alkaloids: protoveratrine, $C_{32}H_{51}NO_{11}$, an extremely powerful poison, and protoveratridine, $C_{26}H_{45}NO_8$, in a very minute amount (ca. 0.001 per cent.). In isolating these alkaloids two methods of extraction were followed. One, the baryta method, is relatively rapid and gives jervine, rubijervine and protoveratridine but no protoveratrine. The other, the metaphosphoric acid method, yields protoveratrine and pseudojervine with small amounts of jervine and rubijervine.

The constitutions of these alkaloids, however, have not yet been investigated. Moreover, the material produced in this country does not appear to have been studied previously and this group of medical plants⁽⁷⁾ occurs in the various species indigenous to this island, Hokkaido, and is fortunately found everywhere in the field. *Veratrum grandiflorum* Loes. fil.⁽⁷⁾, former-

(1) *Ann. Chim. Phys.*, (2), **14** (1819), 69.

(2) *Pogg. Ann.*, **41** (1837), 569.

(3) *Ann. Chem. Pharm.*, **35**, 116.

(4) *Pharm. J. Trans.* April 13, (1878) p. 808.

(5) *J. Chem. Soc.*, **33** (1878), 338; **35** (1879), 405, 421.

(6) *Arch. Pharm.* **228** (1890), 462.

(7) K. Miyabe and Y. Kudo, *J. Coll. Agric. Hokkaido*, **26** (1932), 311.

ly described as *Veratrum album*, is also widely distributed in the mountainous districts of Hondo.

The roots for this investigation were collected at Nopporo, a suburb of Sapporo, in the autumn. As in the course of the preliminary test of extraction the odour of a comparatively lower member of fatty acids, an indication of saponification, was recognized, acid or alkaline extraction applied by former authors was avoided.

The finely powdered roots were percolated with alcohol at room temperature, distilling off the solvent under reduced pressure, and shaking the faintly acid aqueous extract with light petroleum to remove oily and resinous matters. On basifying the aqueous liquor with ammonia or sodium bicarbonate brown basic substances were separated and collected, **portion A**. The filtrate, containing some more alkaloids, was extracted with chloroform after saturation with ammonium sulphate, and amorphous bases were obtained, **portion B**. The crude bases thus obtained were next treated with the usual organic solvents for fractional crystallisation and it was found that ethyl acetate and carbon tetrachloride were the solvents for the purpose but not quite suitable. Attention was then directed to the fractional precipitation and the bases, **portion A** as well as **B**, were dissolved into dilute acetic acid and divided into six fractions with ammonia. On neutralisation of each fraction of **portion A** and **B** with hydrochloric acid, the first three of **portion A** gave only jervine hydrochloride in a crystalline condition, but no crystalline alkaloid was obtained from each fraction of **portion B**. Unfruitful attempts were made to obtain a crystalline substance from the amorphous part by formation of salts, using a variety of acids, organic as well as inorganic.

Since pseudojervine, rubijervine, protoveratrine and protoveratridine which are stated by former authors to have been isolated from European sources in a crystalline condition could not be obtained, the method of isolation after Salzberger⁽⁶⁾ was repeated.

It was found, however, that the material used for this investigation was different from the European, and jervine was so far the only crystalline alkaloid in the material.

The amorphous base of **portion B** was next hydrolysed in a sealed tube with the expectation of obtaining a crystalline hydrolysed base but the results were unsuccessful. On heating with water under pressure or with alcoholic potash, the amorphous base underwent hydrolysis into another amorphous base and angelic acid. On hydrolysis with concentrated hydrochloric acid, the same base gave tiglic acid. The hydrolysis of a veratrum alkaloid, cevadine or crystallised veratrine, is described in the literature,

with different results. Cevadine was first hydrolysed by Wright and Luff⁽⁸⁾ who obtained tiglic acid on hydrolysis with alcoholic soda or with water under pressure but Bosetti⁽⁹⁾ secured angelic acid by alcoholic baryta. The latter suggested that angelic acid was the first product of the hydrolysis of veratrine, and is subsequently converted into tiglic acid. Some years later Ahrens⁽¹⁰⁾ repeated the hydrolysis with alkali and concentrated hydrochloric acid and obtained angelic acid in the case of alkali and tiglic acid in the other case, thus supporting the suggestion of Ahrens.

Freund and Schwarz⁽¹¹⁾, however, obtained angelic acid as well as tiglic acid on hydrolysing the same alkaloid with alcoholic potash. Recently Horst⁽¹²⁾ tried the hydrolysis, passing hydrogen chloride into an alcoholic solution of cevadine, and isolated ethyl tiglate, which, on hydrolysis, gave tiglic acid. It is stated that the tiglic acid is not a product from the angelic acid first formed.

On repeating the hydrolysis of the crude base from *Veratrum grandiflorum* Loes. fil. after Horst, tiglic acid was obtained; it appears that angelic acid is the product first formed in the hydrolysis as has been suggested already by Bosetti⁽⁹⁾ and Ahrens⁽¹⁰⁾ because of the easiness with which angelic acid is convertible into tiglic acid. On the other hand, tiglic acid is so stable that isomerisation did not take place on treatment with water at 120°C. in a sealed tube.

Experimental.

Extraction of the Alkaloids. One part of finely powdered material, collected at Nopporo in October and dried in the sun, was kept in a percolator with two parts of alcohol (95%) and was allowed to stand at room temperature for several days. During the extraction it was shaken at least once a day. The solvent distilled off under reduced pressure, the temperature of the water-bath being kept under 50°C., until practically the whole had been removed, leaving a semi-solid residue. The extraction was repeated with the recovered alcohol. On treating the residue with water and light petroleum (b. p. 40–60°C.) a considerably large amount of dark resinous matter separated and was filtered off. The extract, being faintly acidic, was further shaken with light petroleum several times and finally bubbled with air, when some more resinous matter separated. After filtering off the

(8) *J. chem. Soc.*, **33** (1878), 335.

(9) *Arch. d. Pharm.*, **221** (1883), 87.

(10) *Ber. Deutsch. chem. Gesell.*, **23** (1870), 2703.

(11) *Ber.*, **22** (1899), 800.

(12) *Chem. Zeit.*, **22** (1902), 334.

latter, the brown solution was rendered slightly alkaline with a solution of 6 N-ammonium carbonate. The yellowish brown bases separated were collected, **portion A**, washed, and dried over fresh conc. sulphuric acid in a vacuum desiccator. With ammonium sulphate the mother liquor was salted out and shaken with chloroform. The chloroform solution was dried over anhydrous sodium sulphate, the solvent distilled off thoroughly, leaving an amorphous solid, **portion B**. From the dark resinous matter separated on dilution of the semi-solid residue with water some more alkaloids could be extracted best with dilute acetic acid. The light petroleum which had been used to remove the oily substance from the aqueous extract gave also a little more of the alkaloids by treating with 1 per cent. hydrochloric acid. The yield of the crude alkaloids is 1.2–1.5% referring to the material as shown in the following table :

Material: 12 kg.; alcohol (95%) 24 L.					
Number of extraction		I	II	III	IV
Days percolated		3	6	6	10
Aqueous extract	{ portion A in gr.	45	23	19.5	5.5
	{ portion B in gr.	26.0	16.5	17.0	6.2
Acetic acid extract	{ portion A in gr.	7.1	2.6	0.8	0
	{ portion B in gr.	7.5	1.5	0	0
Hydrochloric acid extract		1.5	0	0	0
Total yield in gr.		87.1 + 43.6 + 37.3 + 11.7 = 179.7			

Isolation and Purification of the Bases. Crude alkaloids obtained by the foregoing method are easily soluble in methyl and ethyl alcohol and are soluble in ethyl acetate and acetone, but very sparingly soluble in ether, chloroform, light petroleum, benzene and carbon tetrachloride.

Attempts to fractionate individuals by taking advantage of differing solubilities in solvents were unsuccessful. With carbon tetrachloride jervine was isolated in a crystalline condition but was not satisfactory.

A suspension of the crude alkaloids, **portion A** (10 gr.) in carbon tetrachloride (1000 gr.) was boiled under a reflux condenser for an hour, filtered, and the filtrate concentrated. On allowing to stand overnight in the ice-chest a brown crystalline powder separated which was collected. Yield was 0.79 gr. The insoluble part was treated with the recovered solvent repeatedly, and the crystalline powder (0.25 gr.) was obtained. On recrystallisation of the crystalline substance thus obtained with methyl alcohol, colourless needle crystals, melting at 242°C., separated. These were collected and proved to be jervine.

The insoluble part (7.5 gr.) was treated with solvents but was not crystallisable and was next made acidic with alcoholic hydrochloric acid. On

keeping in the cold, jervine hydrochloride crystallised in colourless stout prisms which were collected, washed with alcohol, and dried. Weight 0.03 gr.; m. p. 308°C. (with decomposition). The crude base, portion B, was also treated with carbon tetrachloride as in the former case. On extraction of the portion B (5 gr.) with the solvent (500 gr.) a comparatively soluble matter (2.85 gr.) was obtained but could not be obtained in a crystalline condition. This fraction soluble in carbon tetrachloride was then converted into hydrochloride, hydrobromide, oxalate, benzoate and acetate, but did not crystallise. From the fraction of portion B insoluble in carbon tetrachloride no crystalline individual was obtained.

Separation by Fractional Precipitation. *Portion A.* Crude alkaloids (40 gr.) were dissolved into 0.25 N-acetic acid (240 c.c.) and were fractionarily precipitated with 0.5 N-ammonium hydroxide solution (120 c.c.) dividing into five parts. The first fraction was small in amount, coloured brown and mixed with resinous matter, but the amounts of the second fraction and the third were increased rapidly. The weights of the fourth and the fifth fraction were decreased gradually. The mother liquor of the fifth fraction was salted out with ammonium sulphate and was shaken with chloroform. The chloroform solution was washed with a small amount of water and dried over anhydrous sodium sulphate. The solvent was distilled off as completely as possible, leaving a solid mass. This was the sixth fraction.

Each fraction thus obtained was then in turn converted into hydrochloride with 0.1 N-alcoholic hydrogen chloride. On allowing to stand for a while jervine hydrochloride separated from the first, second and third fractions, was collected and dried. Yield 6.71 gr. or 0.13% of the material. In the following table the yield of the salt from each fraction is shown.

Number of fraction	I	II	III	IV	V	VI
Precipitates in gr.	1.62	15.35	7.90	0.77	0.67	10.00
Jervine hydrochloride in gr.	0.55	4.15	2.11	0	0	0

On concentration of the mother liquor of jervine hydrochloride some more salt separated which was removed as completely as possible and the uncrystallisable hydrochlorides of each fraction, which are the greater part of the crude bases, were set free. From these parts neither a free base nor a salt such as sulphate or aurichloride was obtained in a crystalline condition.

Jervine Hydrochloride. The salt is very sparingly soluble in absolute alcohol or water but soluble in dilute alcohol and crystallises in colourless prisms which melt at 308°C. with decomposition.

According to Salzberger⁽⁶⁾ jervine hydrochloride crystallised from alcohol contains two molecules of water of crystallisation but it is now shown that

Anal.: Subst. = 4.195, 4.292, 4.288; CO_2 = 11.635, 11.889, 11.876; H_2O = 3.470, 3.555, 3.575 mg.

Subst. = 4.270 mg.; N_2 = 0.120 c.c. at 16°C. and 764 mm.

Subst. = 4.765 mg.; N_2 = 0.143 c.c. at 18°C. and 766 mm.

Found: C = 75.64, 75.55, 75.54; H = 9.26, 9.27, 9.33; N = 3.34, 3.55%.

Calc. for $\text{C}_{26}\text{H}_{37}\text{NO}_3$: C = 75.86; H = 9.07; N = 3.41%.

Jervine contains no methoxyl group and is laevorotatory, having the following specific rotation which has not been described previously.

$$[\alpha]_{\text{D}}^{19} = \frac{-0.30 \times 100}{0.169 \times 1} = -177.5^\circ \text{ (in absolute alcohol).}$$

Jervine Acetate. This salt was prepared with the object of obtaining an easily soluble salt but it was very unstable against water or heat. On dissolving in water or heating in vacuo the free base was recovered instantly in a pure condition. Jervine in absolute alcohol was neutralised with acetic acid in the same solvent and the resulting solution was evaporated in the desiccator over concentrated sulphuric acid and finally over potassium hydroxide, leaving a colourless crystalline mass which melted at 234–238°C., indefinitely.

Attempts to recrystallise the salt from water, dilute alcohol, alcohol and ether, and other usual organic solvents were made with unfruitful results owing to the easiness with which the acetate decomposed into the original base.

Anal.: 10.427 mg. of air-dry crystals lost at 125°C. and 15 mm. 1.424 mg.

Found: $\text{CH}_3\text{COOH} \cdot \frac{1}{2}\text{H}_2\text{O}$ = 13.66%.

$\text{C}_{26}\text{H}_{37}\text{O}_3\text{N} \cdot \text{CH}_3\text{CO}_2\text{H} \cdot \frac{1}{2}\text{H}_2\text{O}$ requires 14.37%.

Subst. = 3.718, 3.461; CO_2 = 9.516, 8.855; H_2O = 2.784, 2.572 mg.

Found: C = 69.82, 69.78; H = 8.38, 8.31%.

Calc. for $\text{C}_{26}\text{H}_{37}\text{O}_3\text{N} \cdot \text{CH}_3\text{CO}_2\text{H} \cdot \frac{1}{2}\text{H}_2\text{O}$: C = 69.95; H = 8.81%.

The salt is also laevorotatory:

$$[\alpha]_{\text{D}}^{20} = \frac{-0.55 \times 100}{0.4339} = -126.8^\circ \text{ (in absolute alcohol).}$$

Portion B. This was also fractionarily precipitated and converted into hydrochlorides as in the case of portion A, but neither base nor hydrochloride could be obtained in a crystalline condition.

Number of fraction	I	II	III	IV	V	VI
Precipitates in gr.	1.00	7.15	3.85	1.60	6.0	15.50
Jervine hydrochloride	0	0	0	0	0	0

Hydrolysis of the Crude Base, Portion B. With Water. The crude base (5.0 gr.) was heated in a sealed tube with water (100 c. c.) at 120°C. for five hours when an acidic solution, coloured dark brown and partly charred, was obtained. To the filtered solution 1N.-sulphuric acid (10 c. c.) was added

and subjected to steam distillation. The distillate was neutralised with caustic soda and evaporated, leaving a colourless mass (0.54 gr.). From the salt the free acid was prepared, and was crystallised from water in colourless prisms, melting at 46°C ., and was identified as angelic acid.

Silver salt was prepared, melting at 196°C . with decomposition.

Subst. = 4.692; Ag = 2.45 mg. Found : Ag = 52.02%.

Calc. for $\text{C}_5\text{H}_8\text{O}_3\text{Ag}$: Ag = 52.17%.

With Alcoholic Potash. Crude base (20 gr.) was dissolved in alcohol (80 c. c.) and was heated on the water-bath for twenty minutes with caustic potash (10.4 gr.) in alcohol (80 c. c.). On cooling, the reaction product was separated, filtered. The filtrate was saturated with carbon dioxide, separating potassium carbonate. The latter was removed and the solution was concentrated under diminished pressure, leaving a brown powder. After dissolving in water, it was filtered, acidified with sulphuric acid, and extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and the solvent was distilled off, when a crystalline substance remained. The acid crystallised from water in colourless prisms, melting at 45°C ., and was identical with angelic acid. Yield after recrystallisation 0.14 gr.

With Concentrated Hydrochloric Acid. The hydrolysis was made after Ahrens.⁽¹⁰⁾ The same crude base (20 gr.) was heated on the wire gauze for an hour with concentrated hydrochloric acid (50 c. c.). At the early stage of the reaction a reddish brown substance separated, which converted into a dark homogeneous solution on further heating. The reaction mixture was cooled, treated with water (360 c. c.) and was then shaken with ether. After drying the ethereal solution the solvent was distilled off, leaving a crystalline substance (0.31 gr.). This was recrystallised from water in colourless plates, m. p. 64°C ., and was identified as tiglic acid.

3.767 mg. substance required 1.86 c.c. $1/50$ N-NaOH.

Calc. for $\text{C}_5\text{H}_8\text{O}_2$,, 1.88 c.c. ,, .

With Alcoholic Hydrogen Chloride. The same crude base was hydrolysed after Horst⁽¹²⁾ as follows. Crude base (20 gr.) was dissolved in absolute alcohol (75 c. c.) and the resulting solution was boiled on the water-bath for four hours. In the course of heating dry hydrogen chloride was passed through the solution. The alcohol was distilled off when a reddish brown liquid (ca. 1.2 c. c.), having a pleasant smell, together with a crystalline substance, remained. The latter was identified as tiglic acid; the former was treated with alcoholic potash, the hydrolysis being completed by heating for a short time. On distilling off the solvent the residue was acidified,

extracted with ether and the ethereal was dried. From the ethereal solution tiglic acid was obtained, melting at 64°C.

Tiglic acid (10 mg.) was heated with water (0.5 c.c.) in a sealed tube at 120–130°C. for five hours. On cooling tiglic acid (4.5 mg.) separated, and was recovered, m. p. being 61–63°C.

Attempts were made to obtain the hydrolysed base in a crystalline condition but neither the free base nor the salt, hydrochloride, hydrobromide, or perchlorate, could be obtained in a pure condition.

The hydrolysis of each fractionated part of the portion B also gave the same results.

The Metaphosphoric Acid Process for Extraction after Salzberger. After treating the finely powdered material (14 kg.) with ether to remove the oily substance, it was percolated with alcohol (80%) at room temperature. The percolate was concentrated under reduced pressure, the bath temperature being kept below 40°C., when a syrupy substance remained. The latter was further shaken with light petroleum (b. p. 40–60°C.), treated with 0.5 N.-acetic acid, and was then filtered. To the filtrate powdered metaphosphoric acid was added until no further precipitation occurred. The yellow amorphous precipitates, which should contain jervine and rubijervine, were collected, dried and powdered. A suspension of this powder in alcohol was treated with ammonia and was then acidified with sulphuric acid. On warming on the water-bath the sulphate of jervine, which is very sparingly soluble in water, was collected. The mother liquor was again basified with ammonia and was next extracted with ether, but rubijervine could not be found.

The filtrate of the yellow amorphous precipitate was repeatedly extracted with ether and then with chloroform.

On evaporating the ethereal solution a small amount of crude jervine remained but not protoveratrine.

The chloroform solution was also concentrated under reduced pressure, the bath temperature being kept under 40°C., leaving an amorphous substance. The latter was crystallised from absolute alcohol and was identified as jervine instead of pseudojervine.

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SYNTHETISCHE VERSUCHE MIT METHYL-TRIOXYBENZOL. MITTEILUNG I. SYNTHESE VON 2.6-DIMETHYL- POLYOXY-FLAVANONEN.

Von Shin-ichiro FUJISE und Sekio MITUI.

Eingegangen am 10. November 1933. Ausgegeben 28. Januar. 1934.

2.4-Dimethyl-phloroglucin wurde durch Kalischmelze aus Matteucinol bzw. Desmethoxy-matteucinol gewonnen.⁽¹⁾ Zur Konstitutionsermittlung dieser Substanzen synthetisierte der Verf. 5.7-Dioxy-6.8-dimethyl-4'-methoxy-flavanon und 5.7-Dioxy-6.8-dimethyl-flavanon.⁽²⁾ Im folgenden seien Versuche über die Synthese zweier neuer Dimethyl-polyoxy-flavane mitgeteilt. Bei der Kondensierung von Piperonyl-akrylsäure-chlorid und Dimethyl-phloroglucin in Nitrobenzol-lösung unter Zusatz von Aluminium-chlorid erhielten wir 5.7-Dioxy-6.8-dimethyl-3'.4'-methylenedioxy-flavanon ($C_{18}H_{16}O_6$. I.) vom Schmelzpunkt $207^{\circ}C$., das aus 70%iger Essigsäure in hellgelben Nadeln kristallisiert. 5.7-Dioxy-6.8-dimethyl-3'-methoxy-4'-oxy-flavanon ($C_{18}H_{18}O_6$. II) vom Schmelzpunkt $254.5-255^{\circ}C$. wurde durch Kondensation von Dimethyl-phloroglucin und 3-Methoxy-4-carboäthoxy-zimmtsäurechlorid gewonnen.

Die Ausbeute bei diesen Flavanon-Synthesen ist sehr schlecht, weshalb wir keine Derivate, (z.B. Acetylverb., Methyläther) darstellen konnten. Doch erscheint es uns sicher, dass die von uns dargestellten Substanzen Flavanone sind, da sie charakteristische Flavanoneigenschaften zeigen. Bei der Reduktion mit Magnesium und Salzsäure färbten sich beide Substanzen rot. Die Absorptions-spektrum sind ganz analog dem des 5.7-Dioxy-6.8-dimethyl-flavanons.

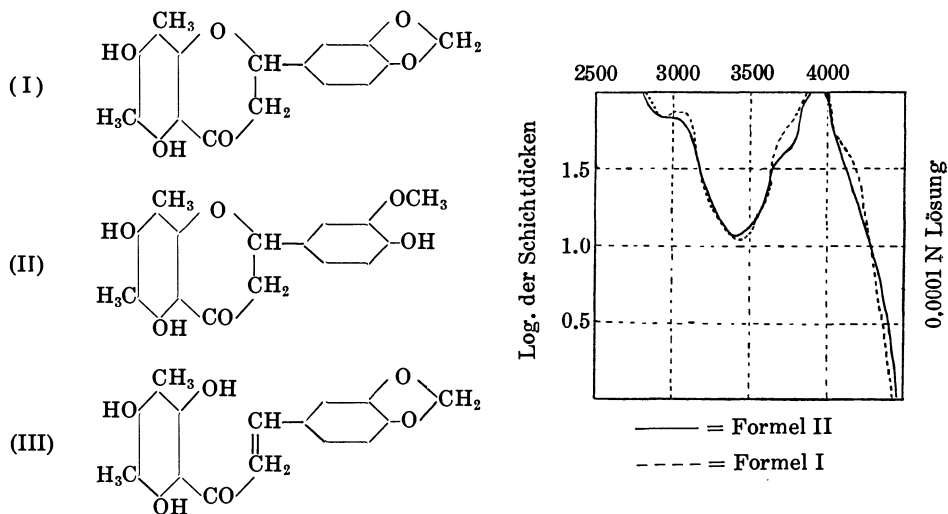
Dimethyl-phloroglucin wurde nach der Anweisung von Weidel und Wenzel⁽³⁾ dargestellt, jedoch mit unbefriedigender Ausbeute. Trinitro-xylool wurde in Eisessiglösung katalytisch reduziert und das Reaktionsgemisch ohne Isolierung von Triamido-xylool mit viel Wasser gekocht. Die Ausbeute an Dimethyl-phloroglucin betrug etwa 30% der Theorie. Zur Synthese von 5.7-Dioxy-6.8-dimethyl-3'-methoxy-4'-oxy-flavanon stellen wir Carboäthoxyferulasäure⁽⁴⁾ nach Shinoda's Vorschrift her. Für die Säure ist, wohl in folge eines Druckfehlers, der Schmelzpunkt als $188^{\circ}C$ angegeben. Er liegt aber bei $178^{\circ}C$.

(1) Fujise, *Sc. Pap. Inst. Phys. Chem. Res.*, **11** (1929), 111; vgl. C. 1930, I. 263.

(2) Fujise u. Nishi, *Ber.*, **66** (1933), 929.

(3) Weidel, *M.* **19** 237.

(4) *J. Pharm. Soc. Japan*, **1929**, 74.



Beschreibung der Versuche.

2.4-Dimethyl-phloroglucin. 1 gr. Pt-oxyd wurde in 100 ccm Eisessig aufgeschlämmt in Wasserstoffatmosphäre geschüttelt und dann 10 gr. fein gepulvertes Tri-nitro-xylol zugesetzt. Während der Reduktion löste sich das Tri-nitro-xylol in Eisessig. Nach 1½ stündigem Schütteln hatte die Lösung 7.71 Wasserstoff absorbiert (92% der Theorie). Das Pt-Schwarz wurde filtriert, das Filtrat mit 10 ccm konz. Salzsäure gemischt und die Lösung im Vakuum eingengt. Der Rückstand wurde mit viel Wasser verdünnt und in Kohlensäureatmosphäre 29 Stunden lang gekocht. Dann wurde, wieder im Vakuum eingengt, das Dimethyl-phloroglucin in Äther aufgenommen und eingedunstet. Nach Verjagen des Äthers wurde der Rückstand aus Xylol umkristallisiert. Schmelzkunkt: 162–163°C. Ausbeute: 29% der Theorie. Die maximum Ausbeute an Dimethyl-phloroglucin nach Weidel und Wenzel betrug 30%. Der Mittelwert war 12% der Theorie.

5.7-Dioxy-6.8-dimethyl-3'.4'-methylendioxy-flavanon (I). 2 gr. Dimethylphloroglucin, 3.45 gr. Piperonyl-akrylsäurechlorid und 4 gr. Aluminiumchlorid wurden zusammen in Nitrobenzol gelöst. Die Lösung färbte sich rot bis dunkelrot. Am nächsten Tage wurden weiter 2 gr. Aluminiumchlorid zugestzt und dies über Nacht stehen gelassen. Dann wurde aus dem Reaktionsgemisch das Nitrobenzol mit Wasserdampf abdestilliert und der Kolbenrückstand heiss dekantiert. Der rotbraune, harzige Rückstand wurde in verdünnter alkoholischer Natronlauge gelöst und nach Zusatz von viel Wasser filtriert. Aus dem Filtrat liess sich mit Kohlensäure die pheno-

liche Substanz ausfällen. Sie wurde zentrifugiert, getrocknet und mehrmals aus 70%iger Essigsäure umkrystallisiert. Ausbeute: 0.2 gr. Schmelzpunkt: 207°C.

Anal.: Subst. = 4.321, 4.179; CO_2 = 10.396, 10.034; H_2O = 1.756, 1.895 mg.

Gef.: C = 65.62, 65.49; H = 4.49, 5.07%.

Ber. für $\text{C}_{18}\text{H}_{16}\text{O}_6$: C = 65.8; H = 4.9%.

Aus der heiss dekantierten Lösung schieden sich Kristalle ab. Beim Waschen mit Natrium-bicarbonat blieb die phenolische Substanz ungelöst, dann wurden sie aus 20%iger Essigsäure umkrystallisiert, und die hellgelben Täfelchen schmolzen bei 222-223°C. Die Analysenergebnisse stimmen zur Formel $\text{C}_{18}\text{H}_{16}\text{O}_6$. Die Verbindung zeigte jedoch kein Flavanonreaktion, also dürfte wohl ein Chalkon (III) vorliegen.

Anal.: Subst. = 3.278; CO_2 = 7.863; H_2O = 1.498 mg.

Gef.: C = 65.41; H = 5.04%.

Ber. für $\text{C}_{18}\text{H}_{16}\text{O}_6$: C = 65.8; H = 4.9%.

5.7-Dioxy-6.8-dimethyl-3'-methoxy-4'-oxy-flavanon (II). 2 gr. Dimethyl-phloroglucin und 4.8 gr. Carboäthoxy-ferulasäure-chlorid (die freie Säure schmolz bei 178°C.) wurden in 120 ccm Nitrobenzol gelöst, nach Zusatz von 4 gr. Aluminiumchlorid zwei Tage lang beiseite gestellt, wieder 3 gr. Aluminiumchlorid zugesetzt und am nächsten Tage das Nitrobenzol mit Wasserdampf abgeblasen; aus der wässrigen Lösung wurde dann neben unveränderter Carboäthoxy-ferulasäure ein rötlichschwarzes Harz isoliert. Das Harz wurde in 10%iger, heisser, alkoholischer Kalilauge gelöst, mit Wasser verdünnt und filtriert. Beim Sättigen des Filtrats mit Kohlensäure fiel eine kristallinische Substanz aus. Aus der alkoholischen Lösung schieden beim Stehenlassen Kristalle aus, die, mehrmals aus 60%iger Essigsäure umkrystallisiert, hellgelben Nadeln vom Schmelzpunkt 254.5-255.5°C. ergaben. Ausbeute 0.3 gr. Mit Eisenchlorid färbten sie sich dunkelgrün. Mit Magnesium und Salzsäure färbten sie sich kirschrot. Die Kristalle löst sich ziemlich schwer in Äther, Alkohol und Aceton.

Anal.: Subst. = 3.650, 3.732; CO_2 = 8.798, 8.950; H_2O = 1.780, 1.894 mg.

Gef.: C = 65.74, 65.41; H = 5.45, 5.69%.

Ber. für $\text{C}_{18}\text{H}_{18}\text{O}_6$: C = 65.5; H = 5.4%.

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SORPTION OF GAS BY MINERAL. IV. ZEOLITES AND BENTONITE.

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In the first report of this series the results of experiments were described on heulandite and chabazite,⁽¹⁾ in the second report on laumontite,⁽²⁾ and in the third report on silicic acid minerals.⁽³⁾

The present paper describes the experiments on the following minerals: laumontite, stilbite, mordenite, natrolite, apophyllite, analcite, inesite and bentonite. The gases tested were ammonia, carbon dioxide, sulphur dioxide, acetylene, oxygen and hydrogen.

Ammonia has been prepared from aqueous ammonia, carbon dioxide from calcium carbonate and hydrochloric acid, sulphur dioxide from sodium sulphite and sulphuric acid, acetylene from calcium carbide and water, oxygen from potassium permanganate, and hydrogen from zinc and sulphuric acid. These gases have been properly purified by the ordinary procedures.

The apparatus and the method of measurements are quite the same as those which were described in former reports.⁽⁴⁾ The sorptions have been measured at 25°C. and 0°C. under about one atmospheric pressure.

Laumontite. The locality of the mineral is Takashima, Hokkaido, being the same sample which was used in the experiment described in the second report of this series. In the former experiment the sorptions of ammonia and carbon dioxide were measured, while in the present paper those of sulphur dioxide, acetylene and oxygen beside ammonia and carbon dioxide are described.

The mineral has been subjected to evacuation and heated to 200°C. for two and half hours. By this treatment the decrease in weight of laumontite amounts to 10.2%. Then the dehydrated mineral has been kept at 25°C. and the sorption velocity and amount of gases have been measured. The results are given in Table 1.

(1) Sameshima, this Bulletin, **4** (1929), 96.

(2) Sameshima, this Bulletin, **5** (1930), 303.

(3) Sameshima, this Bulletin, **6** (1931), 165.

(4) Sameshima, this Bulletin, **2** (1927), 2; **4** (1929), 97; **5** (1930), 173.

Table 1.
Sorption of Gases by Laumontite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of laumontite in c.c.
NH ₃	0.5	762.6	5.91
	3	762.6	7.65
	13	762.6	9.18
	52	761.8	11.14
	167	750.8	12.89
	396	754.0	14.13
	1380	756.9	15.21
CO ₂	0.5	759.6	0.39
	9	759.6	0.69
	362	758.0	0.78
	1408	759.3	0.98
SO ₂	0.5	764.2	1.33
	25	764.2	1.41
	702	763.4	1.82
	1356	768.7	1.96
C ₂ H ₂	0.5	751.2	1.36
	3	751.2	1.96
	27	750.8	2.29
	420	750.4	2.82
	1200	755.8	3.65
O ₂	0.5	754.0	0.20
	240	754.8	0.70
	1524	760.1	1.02

Stilbite. The chemical composition of stilbite is $(\text{CaNa}_2)\text{Al}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}$. The mineral from Kurokura in Shizuoka Prefecture was used in the present experiments. Sorptions of ammonia at 25°C. by stilbite which was de-watered by various treatments have been measured. The results are given in Tables 2, 3 and 4.

Table 2.

Sorption of Ammonia by Stilbite.

Mode of dehydration : Evacuation for 2.5 hours in ordinary temperature.

Loss of weight by dehydration : 2.21%.

Time in min.	Pressure of NH_3 in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C . by 1 gr. of stilbite in c.c.
0.5	749.9	22.54
3	749.9	39.69
5	749.9	46.55
10	749.9	57.87
25	749.9	72.08
62	749.9	88.54
155	749.9	103.84
346	749.6	116.22
594	749.3	123.13
1410	754.7	128.21

Table 3.

Sorption of Ammonia by Stilbite.

Mode of dehydration : Heating at 100°C . for 2.5 hours under evacuation.

Loss of weight by dehydration : 9.19%.

Time in min.	Pressure of NH_3 in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C . by 1 gr. of stilbite in c.c.
0.5	751.7	20.11
3	751.7	30.98
12	751.7	42.37
30	751.7	51.77
90	751.7	66.88
180	751.5	80.43
360	751.8	93.45
482	751.9	98.18
1540	756.5	112.08

Table 4.
Sorption of Ammonia by Stilbite.

Mode of dehydration : Heating at 200°C. for 2.5 hours under evacuation.

Loss of weight by dehydration : 16.18%.

Time in min.	Pressure of NH ₃ in mm.	Vol. of NH ₃ (N.T.P.) sorbed at 25°C. by 1 gr. of stilbite in c.c.
0.5	757.1	11.66
3	757.1	17.97
10	757.1	25.21
30	757.1	38.32
60	757.1	49.24
100	756.8	58.82
190	756.8	71.79
362	756.6	85.00
653	755.7	94.98
1620	754.1	108.42

Thus the mineral sorbs ammonia in considerable amounts, being greater than silica gel and laumontite, though less than chabazite. We see, moreover, that the sample dehydrated at the lower temperature sorbs the more ammonia. A sample was dehydrated at red-heat under evacuation, the weight loss of which being 17.09%. The sorption of this sample was tested but it sorbed almost no ammonia. One gram of this sample sorbed only 0.26 c. c. of ammonia after 1440 minutes. So it is probable that the constitution of the mineral is destroyed by red-heating.

Sorption of ammonia by stilbite at 0°C. instead of 25°C. has been measured, the result of which being given in Table 5.

Table 5.
Sorption of Ammonia by Stilbite.

Mode of dehydration : Heating at 200°C. for 2.5 hours under evacuation.

Time in min.	Pressure of NH ₃ in mm.	Vol. of NH ₃ (N.T.P.) sorbed at 0°C. by 1 gr. of stilbite in c.c.
0.5	762.3	5.69
3	762.3	11.20
12	762.3	17.98
60	762.3	29.78
240	761.9	47.36
1585	760.0	86.91
4435	759.3	111.75
8800	765.5	121.61
14365	758.1	126.04

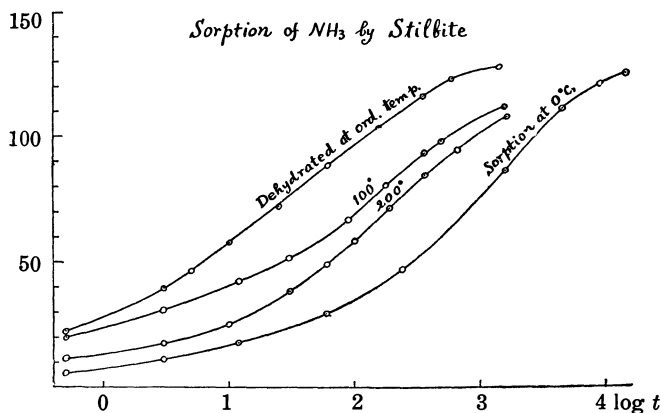


Fig. 1.

The data in Tables 2, 3, 4 and 5 are depicted in Fig. 1, where the volume of ammonia sorbed is taken in ordinate and the logarithm of time in abscissa. As seen from the figure, the sorption velocity at $0^\circ C.$ is smaller than that at $25^\circ C.$, and the amount of ammonia sorbed is nearly the same in two temperatures. From these facts it is probable that the ammonia combines chemically with stilbite. This conclusion is supported by the fact that this mineral sorbs almost no gases in considerable amount except ammonia as shown in Table 6.

Table 6.

Sorptions of Various Gases by Stilbite.

Mode of dehydration : Heating at $200^\circ C.$ for 2.5 hours under evacuation.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at $25^\circ C.$ by 1 gr. of stilbite in c.c.
CO_2	1200	756.0	2.22
SO_2	285	764.1	3.08
C_2H_2	190	753.5	1.41
O_2	1285	754.8	1.48
H_2	1440	764.1	0.69

Mordenite. The composition of mordenite is said to be $3[(K_2, Ca)O \cdot Al_2O_3 \cdot (SiO_2)_{10}] \cdot 20H_2O$. Locality of the mineral used in the present ex-

periments is Arasawa-mura in Iwate Prefecture.⁽⁵⁾ It has white fibrous structure of a few millimeters in length. Some parts have the appearance of glass-wool. Two samples from the same locality were tested.

Sample I. The mineral was dehydrated by heating to 300°C. for 2 hours under evacuation. The loss of weight by this treatment was 9.7%. Sorptions of ammonia and carbon dioxide at 25°C. have been measured on this dewatered sample. The results are shown in Tables 7 and 8, and Fig. 2.

Table 7.

Sorpton of Ammonia by Mordenite.

Time in min.	Pressure of NH ₃ in mm.	Vol. of NH ₃ (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
0.5	755.3	40.30
1	755.3	47.39
2	755.3	52.83
5	755.3	58.84
10	755.3	64.85
30	755.1	74.75
60	755.0	80.60
120	754.5	85.36
1270	754.2	91.86
3010	760.1	92.58
7060	757.3	93.23

Table 8.

Sorpton of Carbon Dioxide by Mordenite.

Time in min.	Pressure of CO ₂ in mm.	Vol. of CO ₂ (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
1	764.5	1.12
5	764.5	2.07
30	764.5	4.40
180	764.5	10.33
450	764.4	15.70
1520	766.8	25.95
4440	759.1	36.28
10200	761.3	43.65
23430	757.5	49.48
60780	751.5	54.15

(5) K. Kawai and K. Kinoshita, *Journal of Geography (Chigaku-Zasshi)*, **41** (1929), 53.
K. Kawai, *ibid.*, **41** (1929), 74.

Sample II. The mineral was dehydrated by heating to 300°C. for 2.5 hours under evacuation, the loss of weight being 11.73%. Sorption of ammonia, carbon dioxide, sulphur dioxide, acetylene, oxygen and hydrogen have been measured. This mineral sorbed large amounts of these gases except hydrogen. No measurable quantity of hydrogen was sorbed by this mineral. The results of measurements are given in Table 9 and Fig. 3.

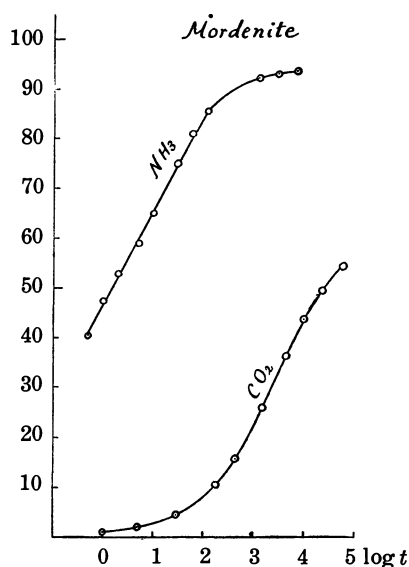


Fig. 2.

Table 9.

Sorption of Gases by Mordenite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
NH ₃	0.5	751.4	117.76
	3	751.4	130.37
	7	751.4	133.29
	60	751.4	133.91
	480	750.8	134.16
	1200	760.2	135.17
CO ₂	1	762.4	6.23
	4	762.4	10.65
	13	762.4	16.10
	32	762.4	23.63
	60	762.4	33.75
	186	763.4	51.02
	612	765.0	69.49

Table 9.—(Concluded)

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
SO ₂	0.5	763.6	10.65
	3	763.6	29.00
	7	763.6	38.93
	12	763.6	46.06
	30	763.6	55.20
	60	763.6	61.29
	125	763.3	67.69
	480	763.9	70.09
	1415	751.1	72.01
C ₂ H ₂	0.5	753.3	0.09
	4	753.3	0.68
	40	753.2	2.98
	120	752.4	5.31
	252	753.3	8.10
	545	754.5	11.52
	721	754.7	13.03
	1410	764.4	14.70
O ₂	0.5	759.0	5.01
	4	759.0	6.87
	11	759.0	7.98
	60	759.0	8.45
	195	759.0	8.73
	625	758.1	9.04
	1448	756.7	9.88

We see from these tables and figures, that the mordenite sorbs various kinds of gases. In this respect, mordenite resembles chabazite and differs from heulandite, laumontite and stilbite. The mechanism of sorption is, therefore, the same as that in the case of chabazite. It is a process of entering gas molecules into the molecular cavities of solid and forms a homogeneous solid solution.⁽⁶⁾ Thus we have found another substance which have the

great capacity of sorbing various gases in addition to charcoal, silica gel, chabazite and meerschaum. Indeed, mordenite may be the second example to chabazite which forms the crystalline molecular sieve.

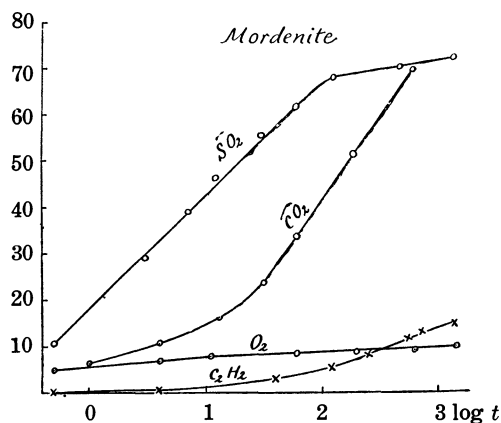


Fig. 3.

(6) Sameshima, this Bulletin, 4 (1929), 125; *Chem. News*, 139 (1929), 61.

Natrolite. The composition of natrolite is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_3 \cdot 2\text{H}_2\text{O}$. The mineral from Tezuka in Nagano Prefecture is used in the experiment. It consists of radial groups of white crystals.

The mineral was dehydrated by heating to 300°C . for 2.5 hours under evacuation. The loss of weight by this treatment was 11.45%. Sorptions of various gases by this substance were measured. The results are given in Table 10.

Table 10.

Sorptions of Gases by Natrolite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C . by 1 gr. of natrolite in c.c.
NH_3	0.5	761.0	0.57
	3	761.0	1.20
	10	761.0	1.90
	65	760.7	3.98
	210	758.3	6.70
	365	757.5	8.37
	1440	755.6	15.75
CO_2	1490	760.4	1.08
SO_2	1440	761.0	0.97
C_2H_2	1380	759.2	1.78
O_2	1320	755.0	0.10
H_2	2880	767.4	0

The natrolite sorbs ammonia slowly, and no other gases. So probably it combines chemically with ammonia.

Apophyllite. The composition of apophyllite is said to be $(\text{H}_{14}\text{K}_2)\text{O}_8 \cdot \text{Ca}_8\text{O}_8 \cdot (\text{SiO}_2)_{16} \cdot 9\text{H}_2\text{O}$. The mineral from Maze in Niigata Prefecture was used.⁽⁷⁾ The mineral was dehydrated by heating to 300°C . for 2.5 hours under evacuation. The decrease in weight was 11.17%. The results of the measurements of sorption on this substance are given in Table 11.

(7) K. Jimbo, *Journal College Science, Imp. Univ. Tokyo, Japan*, **11** (1899), 276.

Table 11.

Sorption of Gases by Apophyllite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of apophyllite in c.c.
NH ₃	0.5	762.3	0.30
	15	762.3	0.48
	140	762.3	1.17
	535	760.1	3.08
	1310	761.3	4.76
SO ₂	1350	764.2	0.63
C ₂ H ₂	1400	759.0	0.89
O ₂	1260	752.6	0.64
H ₂	1260	760.8	0.39

Sorption amounts of gases by apophyllite are thus comparatively small. It seems probable that ammonia combines with the dehydrated mineral, though the amount is lower than other zeolite minerals.

Analcite. The composition of analcite is $(\text{NaAl})\text{O}_2 \cdot (\text{SiO}_2)_2 \cdot \text{H}_2\text{O}$. The mineral from Maze in Niigata Prefecture was used. It was dehydrated by heating to 300°C. for 2.5 hours under evacuation. The decrease in weight was 7.83%. The results of sorption measurements are given in Table 12.

Table 12.

Sorption of Gases by Analcite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of analcite in c.c.
NH ₃	30	761.3	0.39
	450	761.3	0.41
	1440	759.8	0.44
SO ₂	26	758.3	0.45
	180	758.5	0.82
	1140	759.1	1.01
C ₂ H ₂	1	764.6	1.71
	120	764.4	1.89
	1280	771.3	1.95
O ₂	1	764.9	0.32
	1200	756.8	0.32

As is seen from Table 12, no gas is sorbed in considerable quantity by the dehydrated analcite.

Inesite. The composition of inesite is $(\text{Mn, Ca})_6\text{O}_6 \cdot (\text{SiO}_2)_6 \cdot 4\text{H}_2\text{O}$. Zambonini described that the mineral lose 3.85% water on heating to 202°C ., while 5.98% on heating to 310°C . changing the colour of mineral.⁽⁸⁾

The mineral from Rendaiji Mine, Shizuoka Prefecture was used in the present experiments. It is an aggregates of radial groups of pink coloured crystals. The mineral has been dehydrated by heating to 200°C . for 1 hour under evacuation. The loss of weight was 4.84%. Sorptions of ammonia and carbon dioxide were measured. The mineral sorbs considerable amount of ammonia but no carbon dioxide as shown in Table 13.

Table 13.
Sorption of Gases by Inesite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C . by 1 gr. of inesite in c.c.
NH_3	10	767.1	0.91
	60	766.9	1.84
	530	767.2	4.61
	1800	766.8	8.02
	4740	759.9	13.51
	11690	765.2	22.57
	20640	765.9	30.03
	30570	752.8	35.26
	55130	758.1	42.37
	66600	755.7	43.35
	80955	748.9	44.00
CO_2	0.5	756.9	0.15
	43	757.0	0.20
	1200	761.0	0.30

The sorption velocity of ammonia by inesite is rather slow. Non-sorption of carbon dioxide and the slowness of ammonia sorption indicate that the dehydrated inesite combines chemically with ammonia. The dehydrated inesite has nearly been saturated with ammonia after the period

(8) Doelter, "Handbuch der Mineralchemie," Bd. II, 1 Hälfte (1914), 758.

of two months as shown in Table 13. The amount of ammonia sorbed is about 45 c.c. or 0.0020 mol per 1 gram of mineral. The amount of water evaporated by the process of dehydration was 4.84% in our sample, or 0.0027 mol per 1 gram of mineral. Thus the number of mols of the ammonia sorbed is three fourth of that of the water evaporated. The composition of the ammoniacal inesite, therefore, may be $(\text{Mn, Ca})_6\text{O}_6 \cdot (\text{SiO}_2)_6 \cdot 3\text{NH}_3$.

Bentonite. Bentonite is a sort of clay of exceedingly fine grain. It is mainly found in U. S. A. and Canada, and now widely used in industrial purposes. In water it forms a jelly-like mass. It has a strong adsorptive power in aqueous medium. Recently, a substance was found in Japan having similar chemical composition and similar properties with the American bentonite.⁽⁹⁾ The locality of the substance is Yamamoto-mura in Yamagata Prefecture. It is a hard clay of light yellow colour. Sorptive capacities of gases of this Japanese bentonite were measured.

The substance was put in the large quantity of water, stirred and dispersed to form a colloidal solution. The undissolved sandy matter was rejected, and the colloidal solution was evaporated up on a water bath. The dried substance thus obtained, was powdered in an agate motor. The powdered bentonite was then dewatered by heating to 250°C. for 2 hours under evacuation. The sorption of gases were measured on this substance. The results are given in Table 14.

Table 14.
Sorption of Gases by Bentonite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of elutriated bentonite in c.c.
NH_3	0.5	761.8	50.86
	3	761.8	69.16
	10	761.8	76.43
	35	761.0	79.10
	370	753.7	81.13
	1440	759.5	82.30
CO_2	0.5	758.5	4.54
	15	758.5	4.93
	433	758.6	4.95
	1140	758.6	4.98

(9) R. Shigemune, *Tokyo Kogyo Shikensho Hōkoku*, Vol. 25, No. 10, (1930).

Table 14—(Concluded)

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of elutriated bentonite in c.c.
SO ₂	0.5	755.9	12.26
	12	755.9	14.20
	145	751.8	14.60
	1320	749.9	14.97
C ₂ H ₂	0.5	767.8	2.41
	10	767.8	2.81
	185	766.5	2.93
	1542	766.0	3.09
O ₂	1470	760.8	0.29

The bentonite was dispersed in water and the suspensoid was dialysed for 25 days using parchment paper as the dialysing membrane. The substance was evaporated, dried by heating to 250°C. for 2 hours under evacuation. Sorption of gases of this substance have been measured. The results are shown in Table 15.

Table 15.

Sorption of Gases by Dialysed Bentonite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of substance in c.c.
NH ₃	0.5	760.5	42.88
	3	760.5	76.76
	6	760.5	92.23
	30	760.5	104.75
	115	759.4	106.78
	571	762.3	108.48
	1260	763.6	110.39
CO ₂	0.5	763.1	50.04
	3	763.1	89.19
	12	763.1	95.05
	90	763.0	97.00
	300	763.4	97.78
	707	762.9	98.08
	1442	761.6	99.16
SO ₂	0.5	760.5	9.15
	3	760.5	11.16
	35	760.5	12.11
	605	760.7	12.93
	1400	766.6	13.23
C ₂ H ₂	0.5	757.5	1.83
	11	757.5	2.11
	370	756.3	2.41
	1415	758.3	3.19
O ₂	1140	764.9	0.87

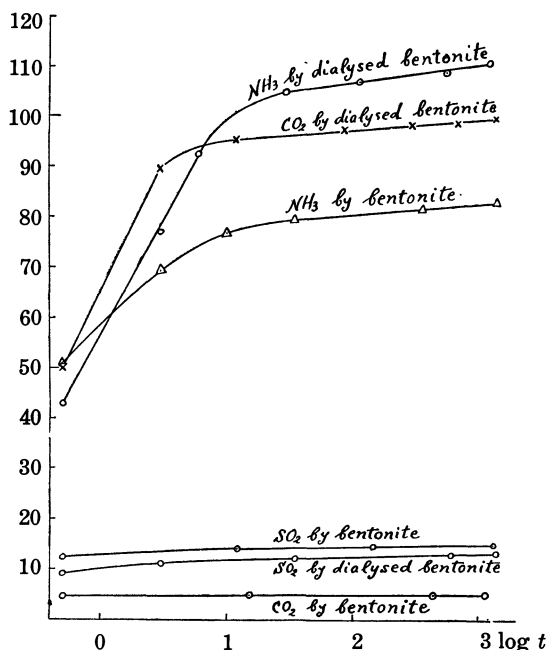


Fig. 4.

The sorption velocities of ammonia, carbon dioxide and sulphur dioxide are depicted in Fig. 4. The curves in the figure are composed of two sections, corresponding to the initial and final sorptions.⁽¹⁰⁾ For the final sorption the following relation holds as shown in the figure :

$$x = k + a \log t,$$

where x denotes the sorption amount at time t , k and a being constants.

The expences connected with this investigation have been defrayed by grants from the Department of Education.

Summary.

1. The sorptions of ammonia, carbon dioxide, sulphur dioxide, acetylene, oxygen and hydrogen under one atmospheric pressure at 25°C. by the dehydrated samples of laumontite, stilbite, mordenite, natrolite, apophyllite, analcite, inesite and bentonite have been measured.

2. All samples except analcite sorb ammonia in considerable quantities.

(10) Sameshima, this Bulletin, 7 (1932), 177.

3. Mordenite sorbs ammonia, carbon dioxide, sulphur dioxide, acetylene and oxygen.

4. Bentonite sorbs ammonia, carbon dioxide and sulphur dioxide.

5. From the sorption amounts of gases and the forms of sorption velocity curves it is concluded that the ammonia combines chemically with laumontite, stilbite, natrolite, apophyllite and inesite.

6. Various gases which are sorbed by dewatered mordenite enter into the cavities among the molecular gratings of mordenite crystals, forming solid solutions. Thus we have found another sorbent of chabazite class.

7. Bentonite is one of the sorbent of silica gel class, being so-called amorphous or microcrystalline structure.

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THE FORMATION OF CYCLIC COMPOUNDS. PART I.
THE RELATIVE EASE OF FORMATION AND
THE RELATIVE STABILITY OF
SIMPLE CARBON RINGS.

By Shin-ichi SAKO.

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It has been shown by Ruzicka and his co-workers⁽¹⁾ that large carbon rings such as, for example, cyclopentadecane, cycloheptadecane and cyclo-octanone, etc. are as stable as five or six membered rings, a fact which does not conform with Baeyer's strain theory. In order to account for this and also for other facts such as the existence of two forms of decahydronaphthalene⁽²⁾ it has been assumed that fully reduced alicyclic structure composed of 6 carbon atoms and more possesses, not uniplanar strained, but multiplanar unstrained configurations. With regard to rings of less than 5-membered, which are supposed to have the atoms lying in one plane, since general experience indicates that they are not as stable as larger rings,

(1) *Helv. Chim. Acta*, **9** (1926), 499.

(2) Hückel and others, *Ann.*, **441** (1925), 1.

Baeyer's conception must still be regarded as correct in so far as the stability of small rings is concerned. On the other hand, it has repeatedly been observed that the strain hypothesis fails completely when applied to explain the relative ease of formation of small strained rings, a fact for which, as far as the author is aware, no satisfactory explanation appears to have been suggested. It is the object of this paper to seek, in a more fundamental manner than has hitherto been done, the cause or causes which affect the ease of formation of simple carbon rings and to present at the same time a view which seems to afford a satisfactory explanation for the facts which the other theories so far put forward fail to explain.

Strictly speaking, in the formation of small rings in particular, it would seem that the comparison of capacity of ring formation simply on the basis of the number of carbon atoms composing rings as has been done by Baeyer and the other workers on this subject is not justified, for there are two cases (A) and (B) in ring formation which, for the reason which will become plain later in this article, must be considered separately :

- (A) The formation of a ring from one molecule of an open chain substance.
- (B) The formation of a ring from more than one molecule of an open chain substance or from more than one substance.

Let us examine, in the first place, the case (A). If a ring is to be formed from a carbon chain, the prime necessity is clearly that the terminal atoms of that chain are to come close together. It follows therefore that the easier the terminal atoms can approach one another, the easier ring formation can take place.

Thus, the fact that rings other than those constituted of 5 and 6 carbon atoms are formed with difficulty would imply that there is some cause or other which makes the coming close together of the terminal atoms of carbon chains other than those composed of 5 or 6 carbon atoms difficult. And since the strain theory of Baeyer fails to explain the facts satisfactorily, it is certain that there is some cause or causes affecting the ease of formation of rings to which no consideration had been given by him. It is one of the fundamental assumptions (or rather the foregone conclusion) in organic chemistry that any two carbon atoms contained in saturated carbon chains can have complete free rotation about the bond, an assumption which means that the relative position of the terminal atoms of all the fully reduced chains except those composed of 2 and 3 carbon atoms is not fixed but alterable in liquid states and in solutions. This is the point to which no attention was paid by Baeyer and Ingold⁽³⁾ and it seems most probable that

(3) *J. Chem. Soc.*, **119** (1921), 305.

the failure of their theories to account satisfactorily for the relative ease of formation of rings had its origin in this, for it would be difficult to suppose that such a nature possessed by carbon chains should not exert any influence on the relative ease of ring formation from them.

Assuming this supposition to be correct, the difficulty with which formation of large carbon rings is attended may be accounted for as follows : although the terminal atoms of carbon chains of upwards of 5-membered may be caused to approach one another by free rotation of the atoms, it would seem reasonable to assume that the larger the number of carbon atoms composing these carbon chains, the slighter there is probability of the terminal atoms coming close together.

The terminal atoms of carbon chains of 3- and 4-membered do not come close together when the angle between the carbon to carbon valencies is normal and the difficulty with which formation of the rings of 3- and 4-membered is attended must undoubtedly be attributed to this fact, although, in the comparison of the ease of formation of these two rings, it would seem that the influence of free rotation of the atoms about the bonds on the relative position of the terminal atoms of the two chains must be considered at the same time. Finally, the terminal atoms of a 2-chain are always in mutual contact, a condition which is unique in all the chains. Doubtless it must be due to this condition that, in spite of the production of the greatest strain which of necessity follows, a 2-ring (a double bond), as has always been observed, is produced with the greatest ease of all rings.

Accepting the views above stated, what has to be taken into account in the comparison of the ease of ring formation from fully reduced carbon chains is, in the case of chains composed of 5 carbon atoms and more, the influence of free rotation of the atoms on the relative position of the terminal atoms and, in the case of chains containing 4 carbon atoms and less, in addition to the above influence, the effect which originates in the production of strain. To make the matter clear, fully reduced open carbon chains may be arranged in four classes according to (i) whether, as a result of free rotation of the atoms, there is a probability of the terminal atoms coming close together (condition X) or not (condition X') and (ii) whether, by free rotation of the atoms, there is a possibility of the relative position of the terminal atoms being altered (condition Y) or not (condition Y'):

	conditions fulfilled
(1) chains of 5-membered and more	X and Y
(2) 4-chain	X' and Y
(3) 3-chain	X' and Y'
(4) 2-chain	(X) and Y'

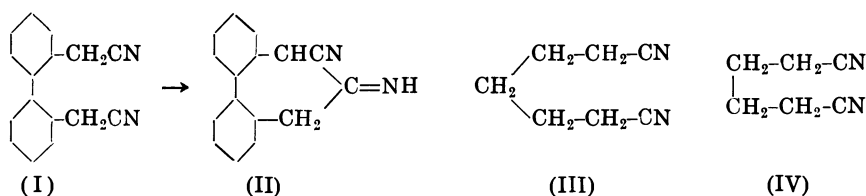
By (X) is meant that a 2-chain possesses the unique condition that the terminal atoms are always in mutual contact. Accepting the assumption already stated, the relative ease of formation of rings from the chains belonging to the class (1), which fulfil conditions X and Y, would solely depend on the number of carbon atoms composing these chains. Thus, a 5-ring should be formed from a 5-chain more readily than a 6-ring from a 6-chain and a 6-ring from a 6-chain more readily than a 7-ring from a 7-chain, etc. An experimental evidence which favors this view was offered by Vogel⁽⁴⁾ who studied slow thermal distillation of adipic, pimelic, suberic, azelaic and sebacic acids, a reaction which satisfied the two conditions required for the comparison of capacity of ring formation, that is, (1) a main reaction involving the formation of the cyclic compound (in this reaction a cyclic ketone) and (2) an alternative side reaction leading to an open chain compound (in this case a saturated monobasic acid), the progress of ring formation in competition with the side reaction being taken as a measure of the ease of ring formation. It was shown that the yields of cyclopentanone and cyclohexanone were respectively 80% and 52% and moreover that the yield of monobasic acid was greater in the pimelic than in the adipic acid series. It was further found that suberic, azelaic and sebacic acids gave good yields of n. heptic, n. octic and n. nonic acids and that the yields of ketone in the first two cases did not exceed 2%.

Experimental verification for the present hypothesis concerning rings composed of more than 7 carbon atoms is difficult to obtain owing to the lack of method of production of these large rings, the only method available at present being that which consists in the dry distillation of the salts of dibasic acids which however, as rightly pointed out by Vogel,⁽⁴⁾ can not be employed to compare ring forming capacity, as the yields of ketone vary with the metal employed.

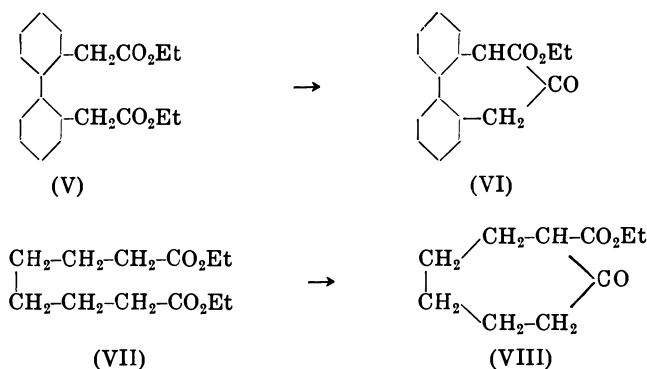
A convincing evidence demonstrating the correctness of the view that free rotation of the atoms composing a saturated chain exercises a great influence on the ease of ring formation is forthcoming from the comparison of the ease of ring formation from the two different states assumed by a given chain, one saturated and the other unsaturated or any state in which free rotation of the atoms is partly inhibited by some means or other. It is to be expected that if the difficulty with which formation of a saturated carbon ring is attended is due to slight probability of the terminal carbon atoms of a chain coming close together as a result of free rotation of the atoms, then it should be possible to remove or to diminish that difficulty by the inhibition of free rotation between some of the atoms constituting that

(4) *J. Chem. Soc.*, **1929**, 722.

chain by such means as the introduction of a double linkage or linkages into the system or otherwise, although it is of course necessary that in the latter form also the terminal atoms can approach each other. As a matter of fact, we find that this is precisely what happens in a 7-chain, for, whilst 7-rings are generally produced from saturated 7-chains with great difficulty, it is a well-known fact that there is no difficulty encountered in obtaining 7-membered rings from certain 2,2'-substituted diphenyls. For example, whilst the compound (II) is readily formed from $\omega\omega'$ -dicyano-2,2'-dimethyl diphenyl (I) under the influence of sodium ethoxide⁽⁵⁾ even derivatives of cyclohexanone can not be prepared from $\alpha\epsilon$ -dicyanopentane (III) by this method⁽⁶⁾ although this condensation occurs readily when applied to $\alpha\delta$ -dicyanobutane (IV), giving rise to the cyclopentane derivative.⁽⁷⁾



Similarly, the compound (VI) is produced in an 80% yield when ethyl 2,2'-dimethyl diphenyl- $\omega\omega'$ -dicarboxylate (V) is treated with sodium,⁽⁸⁾ while under similar conditions ethyl cycloheptanone carboxylate (VIII) is obtained from ethyl suberate (VII) only in a 10% yield.⁽⁹⁾



(5) Kenner, *J. Chem. Soc.*, **99** (1911), 2101.

(6) *J. Chem. Soc.*, **103** (1913), 614.

(7) Thorpe, *J. Chem. Soc.*, **95** (1909), 1901.

(8) Kenner, *J. Chem. Soc.*, **103** (1913), 615.

(9) Dieckmann, *Ann.*, **307** (1901), 50.

Although diphenic anhydride can easily be prepared from diphenic acid by the action of a dehydrating agent, only a very poor yield of adipic anhydride results when adipic acid is similarly treated.

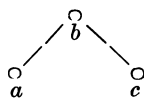
In the formation of 5-rings also, there is evidence to show that a 5-ring is more readily formed from a 5-chain when free rotation of the atoms is partly inhibited than when otherwise. Thus, maleic and phtharic acids on distillation passes quantitatively into the anhydrides, while succinic acid is incompletely converted into the anhydride by the same treatment.⁽¹⁰⁾ It follows therefore that it is not simply the presence, in 2,2'-substituted diphenyls, of four angles of 120° which is larger than the normal angle that is responsible for the ready formation of 7-rings from them, for, if so, succinic acid should give the 5-membered anhydride more readily than phtharic acid in which there are present two angles of 120° involved in the formation of the anhydride. As will again be discussed later in the case of formation of small rings, the fact would seem to be that the production of strain following ring formation is not a factor which affect the ease of ring formation to so great an extent as has hitherto been supposed.

With regard to the relative ease of formation of 2-, 3- and 4-rings, respectively, from 2-, 3- and 4-chains, it has repeatedly been observed that a 2-ring (double bond) is formed more readily than a 3-ring and a 3-ring more readily than a 4-ring, a fact which is not in agreement with the strain theory. On the other hand, general experience indicates that as required by Baeyer's conception a 4-ring is more stable than a 3-ring and a 3-ring more stable than a 2-ring. These observations that the relative ease of formation and the relative stability of the three rings are not parallel would naturally lead one to suppose that, since the relative stability of the rings can be satisfactorily accounted for, at any rate qualitatively, by the strain theory, there should be present in these short chains, in addition to the remoteness between the normal positions of the terminal atoms (2-chains excepted) as assumed in the simple conception of Baeyer and Ingold,⁽⁹⁾ some factor or other which must be taken into account in comparing the ease of ring formation. It seems very probable that as already stated, this factor is one that is brought about by free rotation of the atoms which exercise different influences on the relative position of the terminal atoms of a 4- and a 3-chain belonging to the different classes (2) and (3). And if it is to be accepted that the possibility of free rotation of the atoms does at all affect the ease of formation of large rings from longer chains, there is no reason why the same effect should not play any part in the formation of rings from the short chains. If that is the case, it will be found easy to account for all the

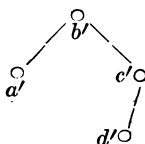
(10) Meyer and Jacobson, "Lehrb. d. Org. Chem." Bd. I. T. II, 362.

known facts concerning the relative ease of formation of strained rings for which no satisfactory explanation appears to have been suggested.

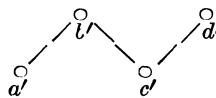
As above referred to, the fact that a 2-ring, which ought to be in the most strained state as required by the strain theory and as reflected by its greatest instability, is actually produced with the greatest ease of all the rings must undoubtedly be attributed to the unique condition, the most favorable to ring formation from the point of view of the present hypothesis, that the terminal atoms are always in mutual contact. At the same time, this fact may be regarded as indicating that the production of strain which follows ring formation cannot be the cause which affect the ease of ring formation to so great a degree as has hitherto been supposed, a matter of importance when considering the relative ease of formation of a 3- and 4-ring. There seems to be no difficulty now to account for the fact that a 3-ring is formed from a 3-chain more readily than a 4-ring from a 4-chain. Thus, whilst a 4-chain belongs to the class (2) fulfilling the conditions X' and Y which both are unfavourable to ring formation, there is present in a 3-chain only one unfavourable condition X' . In the diagrams (IX), (X) and (XA), the carbon atoms a, b, c, a', b', c' and d' composing respectively a 3- and a 4-chain are supposed to be lying in the plane of the paper. In the formation of a 3-ring from a 3-chain (IX) the terminal atoms a and c cannot but come close together merely by the deflection of the angle between the carbon to carbon valencies, for in a 3-chain the relative position of the terminal atoms is not altered by free rotation of the atoms. On the other hand, in a 4-chain, as will be seen in the diagrams (X) and (XA) showing the two cases of arrangements assumable by a 4-chain, in which one is obtained from the other when the atom c' rotates through an angle of 180° , there is a possibility of the relative position of the terminal atoms a' and d' being altered, a condition which is not present in the terminal atoms of a 3-chain. It would be only when a 4-chain assumes the arrangement (X) and also perhaps the arrangements close to (X) that there is any chance of the union of a' and d' taking place. In the arrangements other than those mentioned above it is evident that the mere deflection of the angle between the carbon to carbon valencies cannot bring the terminal atoms a' and d' near together.



(IX)



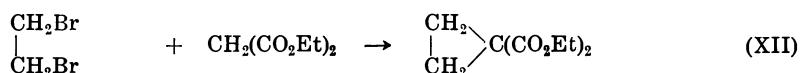
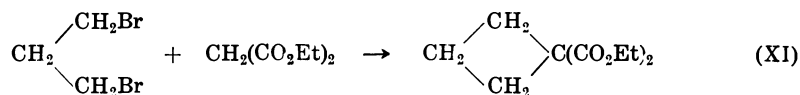
(X)



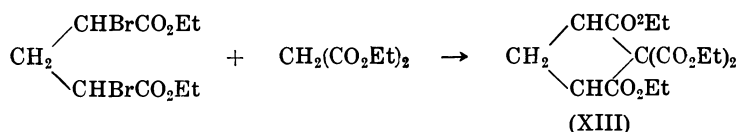
(XA)

In other words, whilst in a 3-chain, there is at any moment a possibility of the closure of a 3-ring, in a 4-chain the arrangement in which there is a possibility of ring formation would on an average be of much shorter duration than that in which there is no possibility of ring formation. In this connection, it should be noted that, although a 4-chain may assume either the arrangements (X), or (XA) or any intermediate state between the two, it is probable that the zigzag arrangement (XA), especially when the terminal atoms a' and d' bear the same grouping (or indeed any two kinds of grouping which possess the same sign of electrical charge), is more stable than (X), since, as is well-known in the cis-trans isomerism, a trans form is more stable than a cis form. And if it is so, this effect may well play part to hinder the closure of a 4-ring. In these circumstances, it would seem that there is nothing strange in the fact that a 3-ring is formed from a 3-chain more readily than a 4-ring from a 4-chain.

Experimental support for the above view is furnished through the comparison of the ease of formation of a 4-ring and a 3-ring respectively from two substances. The examples described below are those which were cited by Vogel⁽⁴⁾ in order to show that the modified theory of Ingold fails to cover all the facts which have been discovered, but which, instead, provide evidence in favour of the present hypothesis. It was found that the cyclobutane compound (XI) was produced in a greater yield than the cyclopropane compound (XII) when trimethylene bromide and ethylene bromide was condensed, respectively, with ethyl sodiomalonate⁽¹¹⁾:

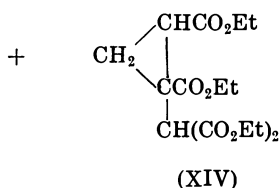


The cyclobutane (XIII) and the cyclopropane (XIV) compounds were obtained in the almost equal yields in the condensation of ethyl $\alpha\alpha'$ -dibromoglutarate with ethyl sodiomalonate in alcoholic solution; condensation in benzene solution gave a 70-80% yield of (XIII)⁽¹²⁾:



(11) Perkin, *J. Chem. Soc.*, **47** (1885), 801; **51** (1887), 1;
Perkin and Prentice, *J. Chem. Soc.*, **59** (1891), 823.

(12) Ing and Perkin, *J. Chem. Soc.*, **127** (1925), 2387.

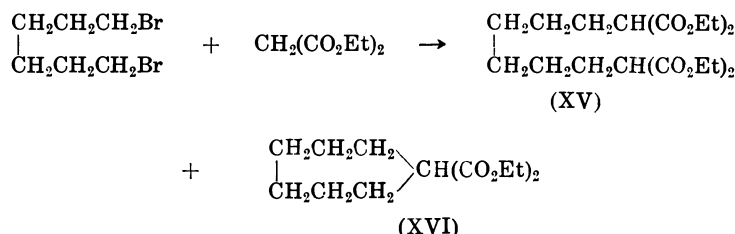


It will be noticed at once that, in each reaction, one molecule each of two substances, a 3-chain in one and an atom in the other, takes part in forming a 4-ring. There seems no doubt that it is due to this fact that, whilst in general a 4-ring is formed from a 4-chain with greater difficulty than a 3-ring from a 3-chain, the cyclobutane compounds (XI) and (XIII) are produced more readily than the cyclopropane compounds (XII) and (XIV) in these reactions.

According to the present hypothesis, no difficulty is encountered in giving a satisfactory explanation for the difference between the two cases. It is evident that, since in the above reactions the relative position of the terminal atoms of a 3-chain is not altered by free rotation of the atoms, the conditions under which the cyclobutane rings (XI) and (XIII) are produced by its combination with the carbon atom in the sodiomalonate are entirely different from those when a 4-ring is formed from a 4-chain, the relative position of the terminal atoms of which is alterable. Thus in the reaction by which the cyclobutane (XI) and cyclopropane (XII) compounds are formed, not only the relative position of the terminal atoms of each of the 3- and the 2-chains contained respectively in trimethylene bromide and ethylene bromide is unalterable, but also the terminal atoms in each chain are so close to one another that the carbon atom in the sodiomalonate is able to approach them simultaneously. The outcome would be that in this reaction the factor which affects the ease of formation of the cyclobutane (XI) as well as cyclopropane (XII) compounds is only the strain which is to be produced, and hence the greater yield of the former (XI). The better yield of the cyclobutane compound (XIII) than the cyclopropane compound (XIV) is also to be ascribed to the same cause.

In the formation of a large ring, however, it will be rare that it is formed from more than one substances without going through an intermediate stage, since in a long carbon chain, the relative position of the terminal atoms of which are alterable, there is slight probability of both terminal atoms of the chain approaching the terminal atoms of the other chain or chains at the same moment. Thus, for example, the condensation of hexamethylene bromide with ethyl sodiomalonate yielded mainly ethyl

octane tetracarboxylate (XV), the cycloheptane compound (XVI) being obtained in a very poor yield.⁽¹³⁾



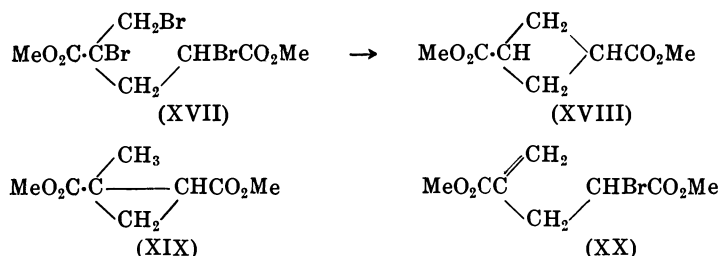
In this reaction, the cycloheptane compound (XVI) must have been produced mostly through the intermediate compound. In that case, the reaction is the same as that in which a 7-ring is formed from a 7-chain.

There seems to be no difficulty now to explain the fact that the relative ease of formation and the relative stability of small rings are not parallel, for, as already mentioned, there is present in the formation of strained rings a factor, other than that which originates in the production of strain, which greatly affect the ease of ring formation. Before ring formation, 4-, 3- and 2-chains belong, respectively, to the different classes (2), (3) and (4) which satisfy different conditions regarding the relative position of the terminal atoms, a fact which imply that the conditions under which the small rings are to be formed from these chains are not comparative. But with the union of the terminal atoms, such a difference as existed between the chains disappears, and 4-, 3- and 2-rings are now under comparative conditions as to their stability, the degree of strain indicating the degree of instability of the small rings.

The rather difficult case in which the closure of a 4-ring occurred very easily from a 4-chain and which is apparently in conflict with the present hypothesis is that when methyl $\alpha\beta\delta$ -tribromobutane- $\beta\delta$ -dicarboxylate (XVII) was treated with zinc, acetic acid and a little water at first in the cold and afterwards on the water bath the quantitative production of cis-cyclobutane-1,3-dicarboxylate (XVIII) and not the cyclopropane compound (XIX) resulted.⁽¹⁴⁾ Perkin and Simonsen concluded from the result that the cyclobutane compound (XVIII) was more readily formed than the cyclopropane compound (XIX) in agreement with the strain theory. It appears however they have overlooked another alternative that there is strong reason to believe that the zinc first of all would attack the $\alpha\beta$ -bromine atoms giving rise to the unsaturated compound (XX) as an intermediate product :

(13) Haworth and Perkin, *J. Chem. Soc.*, **65** (1894), 599.

(14) Perkin and Simonsen, *J. Chem. Soc.*, **95** (1909), 1169.



The compound (XVII) is therefore an interesting substance which, according to the ways of debromination, may yield different compounds containing either a double bond or a 3-ring or a 4-ring. Before considering the probable mechanism of the production of (XVIII) from (XX) some of the previous result on the debromination of various dibromo-compounds by the action of zinc must be given. In this case too, there is a mass of evidence which shows most convincingly that $\alpha\beta$ -dibromo-compounds are very much more easily debrominated yielding unsaturated substances than $\alpha\gamma$ - and $\alpha\delta$ -dibromocompounds.

Thus, for instance, Petrenko-Kritschenko and Konschin⁽¹⁵⁾ studied the debromination velocity of various dibromo alkane. The method employed was to shake the dibromocompounds with zinc dust in alcohol at ordinary temperature. The results obtained after one hour and 6 hours are shown in the table below, the quantities of the dibromoalkane which reacted with zinc being given in percentages :

	1 hr.	6 hr.
ethylene bromide	19.87%	—
$\alpha\beta$ -dibromopropane	20.87 „	53.58%
trimethylene bromide	2.02 „	2.68 „
$\alpha\delta$ -dibromopentane	1.80 „	1.55 „
$\alpha\epsilon$ -dibromopentane	1.25 „	—

It will be seen from the table that (a) the $\alpha\beta$ -dibromocompounds reacted with zinc very much more easily than the others, (b) whilst the quantity of $\alpha\beta$ -dibromopropane which reacted increased greatly with the lapse of time, the quantities of the others after one hour, which are all so negligibly small, are practically the same as those after 6 hours, that is, the reaction stopped after a short time, and (c) with the increase of the number of carbon atoms existing between the bromine atoms, the reaction took place with more difficulty. Again, it was found by Zelinsky and Schlesinger⁽¹⁶⁾ that although on treatment of ethylene bromide with zinc dust and glacial acetic acid a violent reaction took place yielding ethylene, no reaction occurred when

(15) *Ann.*, **342** (1905), 57.

(16) *Ber.*, **41** (1908), 2429.

trimethylene bromide was submitted to the same treatment. They found however that trimethylene bromide reacted with zinc in presence of 50% acetic acid giving rise to cyclopropane but the reaction velocity was very small at ordinary temperature. Hamonet⁽¹⁷⁾ obtained butane on treatment of tetramethylene bromide with zinc and ethyl alcohol. As a matter of fact, the reaction which used to take place when dibromocompounds other than $\alpha\beta$ -dibromocompounds are treated with zinc and acetic acid is, not debromination leading to ring formation, but reduction involving the production of saturated open chain substances.⁽¹⁸⁾ To take a few more examples in which a carboethoxyl group is present, ethyl $\alpha\beta$ -dibromobutyrate gave ethyl crotonate when its ethereal solution was treated with zinc,⁽¹⁹⁾ whereas ethyl $\alpha\gamma$ -dibromobutyrate yielded on treatment with zinc and ethyl alcohol ethyl butyrate.⁽²⁰⁾

These examples cited above are only a few of the numerous facts which have been discovered showing that debromination occurs most easily in the case of $\alpha\beta$ -dibromocompounds. As described above, although trimethylene bromide gives under certain conditions cyclopropane, as far as the author is aware no example is recorded in which a cyclobutane compound is produced from an $\alpha\delta$ -dibromo-compound by the action of zinc and acetic acid.

In view of these facts, there seems no reason why, notwithstanding the presence of the bromine atoms in the $\alpha\beta$ -positions of (XVII), only in the production of (XVIII) from (XVII) the debromination of the $\alpha\delta$ -bromine atoms leading to the formation of the cyclobutane ring should occur in the first phase of the reaction, and since the cyclopropane compound (XIX) was not actually produced, a result which is not surprising, one is forced to conclude that the zinc first of all must have attacked, most probably while cold, the $\alpha\beta$ -bromine atoms of (XVII) giving (XX) as the intermediate product which then, probably when heated, would have passed into (XVIII) through the hypothetical intermediate state (XXI) produced by the elimination of the δ -bromine atom by the action of nascent hydrogen.

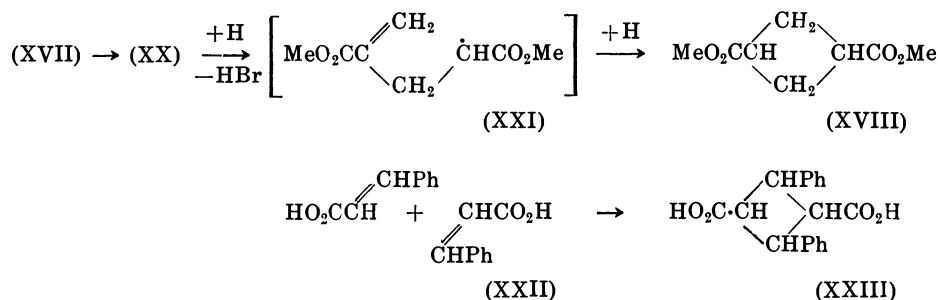
The fact that cinnamic acid (XXII), a derivative of acrylic acid, has a marked tendency to polymerise giving rise to the cyclobutane compound, α -truxillic acid (XXIII), may be taken as an example indicating that somewhat analogous change as the transformation of (XXI), also a derivative of acrylic acid, into the cyclobutane compound (XVIII), of which α -truxillic acid is a diphenyl derivative, is not altogether an unjustifiable supposition.

(17) *Compt. rend.*, **132**, 789.

(18) Compare, Victor Meyer u. Jacobson's "Lehrbuch d. Org. Chem.", Bd. II, T. I, 770.

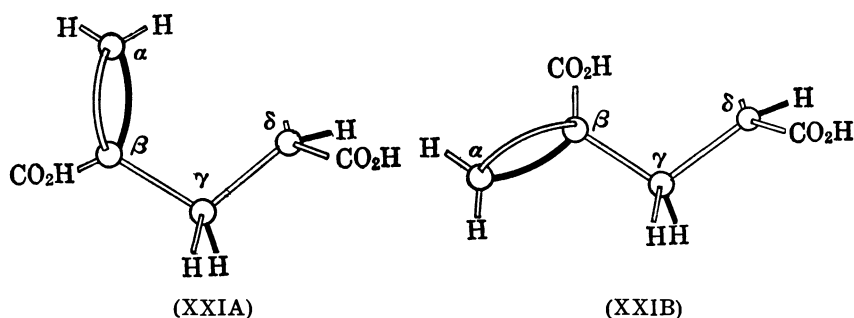
(19) Michael and Schulthess, *J. Pr. Chem.*, **43** (1891), ii, 590.

(20) Kishner, *J. Russ. Phys.-Chem. Ges.*, **41**, 660.



It is also possible that the debromination of the $\alpha\beta$ -bromine atoms by the action of zinc and the removal of the δ -bromine atom by the action of nascent hydrogen might have occurred at the same time, but Zelinsky and Schlesinger⁽¹⁶⁾ stated that in absence of water zinc and acetic acid did not react at all with each other and that even when 50% acetic acid was used the reaction took place with difficulty.

It is interesting to note that, if it is assumed that the production of the hypothetical intermediate state (XXI) is the case, then it follows that there is no possibility of the production of the cyclopropane compound (XIX) from it. In the diagrams (XXIA) and (XXIB) representing the two cases of arrangements which may be assumed by (XXI) (one is obtained from the other when the β -carbon atom rotates through 180°), the α -, β -, γ - and δ -carbon atoms are supposed to be lying at the angular points in the plane of the paper and therefore the plane of the double bond would lie in a plane perpendicular to the plane of the paper. Now, assuming that the production of the hypothetical product (XXI) precedes the formation of the cyclobutane (XVIII) or cyclopropane (XIX) compounds, in order that (XXI) is transformed into (XVIII) as well as (XIX), (XXI) must in the first place have the arrangement (XXIA), for in the other arrangement (XXIB) or in any arrangement representing the intermediate state between (XXIA) and (XXIB) the valencies linking the α - and β -carbon atoms, one of which is required to close the 4- or 3-rings, emanate in the direction where there is no possibility of ring formation. In other words, it is evident that in the arrangement (XXIB) the presence of the carboxyl group carried by the valency emanating in this direction from the β -carbon atom would render the formation of a 3-ring through the $\beta\delta$ -atoms impossible. Again, in the arrangement (XXIA), if the attempt be made to approach the β -carbon atom to the δ -atom, it will be seen that it is, not the β -atom, but the α -atom which is the first to come close to the δ -atom, the formation of the cyclobutane compound (XVIII) by the union of the α - and δ -atoms being thus left as the only possibility.



In view of the large number of facts satisfactory correlated by the present hypothesis it seemed desirable to undertake a series of experiments with the object of examining the more essential points stated in this communication on the causes which seem to affect the ease of ring formation. It is intended to publish the results of the experiments in future papers.

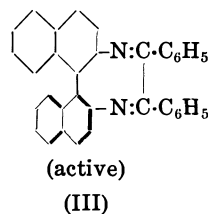
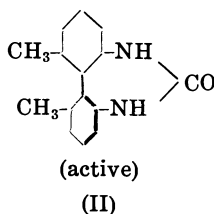
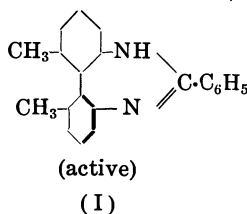
*Chemical Department, Faculty of Engineering,
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THE FORMATION OF CYCLIC COMPOUNDS FROM DERIVATIVES OF DIPHENYL. PART II.⁽¹⁾ THE FORMATION OF 4, 5, 9, 10-DIBENZOPYRENE AND 4, 5-DIPHENYLDIPHENYLENE OXIDE FROM 6, 6'-DIPHENYLDIPHENYL-2, 2'-TERAZONIUM SULPHATE.

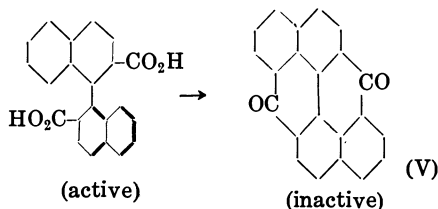
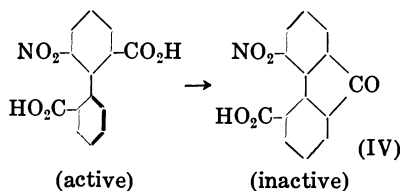
By Shin-ichi SAKO.

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It has been found that 7- or 8-membered rings formed through the 2, 2'-positions of diphenyl compounds assume nonplanar unstrained configurations. This was demonstrated by the fact that when 7- or 8-membered rings were formed through the 2, 2'-positions of certain optically active 2, 2', 6, 6'-substituted diphenyls the products still retained optical activity. Thus, the compounds (I), (II) and (III) produced respectively from *l*-2, 2'-dimethyl-6, 6'-diaminodiphenyl⁽¹⁾ and *d*-2, 2'-diamino-1, 1'-dinaphthyl⁽²⁾ were optically active.



On the other hand, it has been shown by a number of examples that the products obtained by the closure of 5- and 6-membered rings through the 2, 2'-positions of optically active diphenyl compounds are optically inactive. *d*-2-Nitro-6, 6'-dicarboxydiphenyl and *d*-2, 2'-dicarboxy-1, 1'-dinaphthyl, on heating with sulphuric acid, gave respectively the inactive compounds (IV) and (V).⁽³⁾

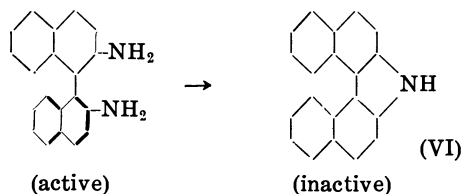


(1) For previous paper see Sako, *Mem. Coll. Eng. Kyushu Imp., Univ.*, **6** (1932), 263.

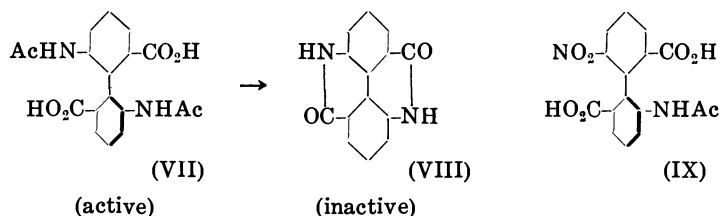
(2) Kuhn and Goldfinger, *Ann.*, **470** (1929), 183.

(3) Bell and Robinson, *J. Chem. Soc.*, **1927**, 2238; Kuhn and Albrecht, *Ann.*, **465** (1928), 282.

Similarly, inactive naphthocarbazol (VI) was obtained by heating either the *d*- or *l*-form of 2, 2'-diamino-1, 1'-dinaphthyl with hydrochloric acid.⁽²⁾



when *l*-6, 6'-diacetamidodiphenic acid (VII) was hydrolysed by cold sulphuric acid an inactive dilactam (VIII) was produced.⁽⁴⁾



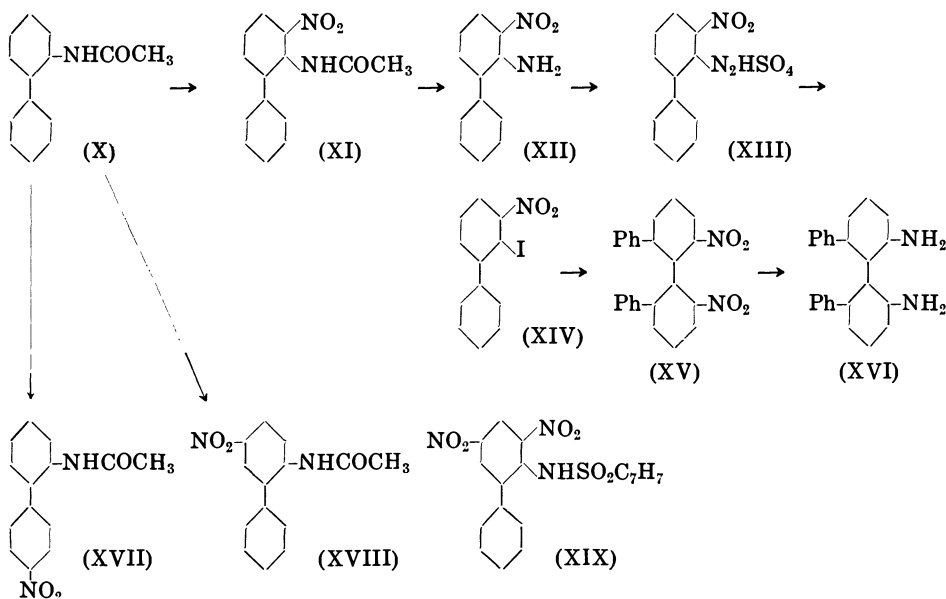
Since most of these active substances are stable toward heat or toward chemical reagent, the disappearance of optical activity is supposed to be due, not to racemization, but to the change from a spatial arrangement to a coplanar structure. But in view of the fact that the formation of all but one of the 5- or 6-membered rings in the above examples was effected by heating and also that such a compound as (VII), the only substance from which ring formation was accomplished in the cold, does not appear to be a suitable substance, for it has been found that the active forms of the compound (IX) which is a somewhat similar substance to (VII) in constitution easily racemizes in hydrochloric acid solution even at ice-cold temperatures (the unpublished result of the author.), it may be stated that the evidence furnished by these examples is not as conclusive as is desirable for demonstrating the correctness of this supposition.

Meisenheimer and Höring⁽⁴⁾ stated that the sodium salt of the active substance (VII) is stable toward heat but this can not be taken as indicating the stability of the free acid, for the author found that the active form of (IX), though not stable as free acid, was stable in the form of its sodium or ammonium salt in similar circumstances. In order to place this supposition on a firmer ground it is desirable to use an active substance which is not

(4) Meisenheimer and Höring, *Ber.*, **60** (1927), 1433.

only quite resistant to racemization but also produces 5- or 6-membered rings through the 2, 2'-positions with ease at as low a temperature as possible. The substance which adequately fulfils these conditions seemed to be 2, 2'-diamino-6, 6'-diphenyl diphenyl (XVI) in which the presence of the phenyl groups would perhaps stabilize the optical isomers. It is to be expected also that the tetrazonium salt prepared from (XVI), judging from its constitution, might decompose in three ways resulting in the formation of either two 6-membered rings or one 5-membered ring through the 2, 2'-positions or of two hydroxyl groups in the 2, 2'-positions. Although the intended object was not attained on account of the fact that attempts to separate 2, 2'-diamino-6, 6'-diphenyl diphenyl into optical antipodes have not so far been unsuccessful, a description of the preparation of this compound (XVI) and the decomposition products of the tetrazonium salt derived therefrom may be of use.

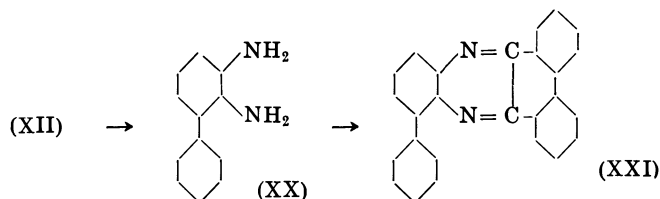
The starting substance for the preparation of 2, 2'-diamino-6, 6'-diphenyl diphenyl was 2-acetamidodiphenyl (X) which on nitration with a specially devised method yielded 3-nitro-2-acetamidodiphenyl (XI). This could be successively converted into 2-amino-3-nitrodiphenyl (XII), its diazonium sulphate (XIII) and 3-nitro-2-iododiphenyl (XIV), and the latter treated according to the Ullmann method with copper powder. 2, 2'-Dinitro-6, 6'-diphenyl diphenyl (XV) produced in this way on reduction gave 2, 2'-diamino-6, 6'-diphenyl diphenyl (XVI):



Two mononitro derivatives of 2-acetamidodiphenyl have been recorded in the literature: one of these, 4'-nitro-2-acetamidodiphenyl (XVII) was obtained as the primary product by acting nitric acid on 2-acetamidodiphenyl in a mixture of sulphuric acid and acetic acid,⁽⁵⁾ while the other, 5-nitro-2-acetamidodiphenyl (XVIII) was obtained in the presence of acetic acid alone.⁽⁶⁾ The only substance recorded, having a nitro-group in the ortho-position to the amino-group, was a dinitro-compound, 3,5-dinitro-2*p*-toluene sulphonamidodiphenyl (XIX).⁽⁶⁾

Applying the method of Witt and Utermann⁽⁷⁾ for the preparation of *o*-nitroaniline which consisted in nitrating the acetanilide in a mixture of acetic anhydride and acetic acid it was found that 3-nitro-2-acetamidodiphenyl could be obtained as one of the two products, the other product being 5-nitro-2-acetamidodiphenyl (XVIII). The Witt and Utermann method thus seems capable of general application for the preparation of similar derivatives of *o*-nitroaniline, for 3-nitro-*o*-toluidine proved also to be obtainable in a good yield from *o*-acetotoluidide by the same method.⁽⁸⁾

The constitution of the 3- and 5-nitro-2-aminodiphenyl thus obtained were confirmed by the examination of their reduction products, the diamino-compounds. 2,3-Diaminodiphenyl (XX) obtained from (XII) on treatment with hydrochloric acid and ferric chloride gave the deep red diaminophenazine derivative and with phenanthrene quinone the 2,3-(*oo'*-diphenylene)-5-phenyl quinoxaline (XXI):



Similarly, 2-amino-5-nitrodiphenyl was converted into 2,5-diaminodiphenyl which showed characteristic reactions of *p*-phenylene diamine.

Although the yield of 3-nitro-2-acetamidodiphenyl (XI) from 2-acetamidodiphenyl was but 22.6% of the theoretical, thanks to the fact that, in the subsequent stages of preparations, 3-nitro-2-iododiphenyl (XIV), 2,2'-dinitro-6,6'-diphenyl diphenyl (XV), and 2,2'-diamino-6,6'-diphenyl diphenyl (XVI) were under favourable conditions all produced in the almost quantitative

(5) Scarborough and Waters, *J. Chem. Soc.*, **1927**, 89.

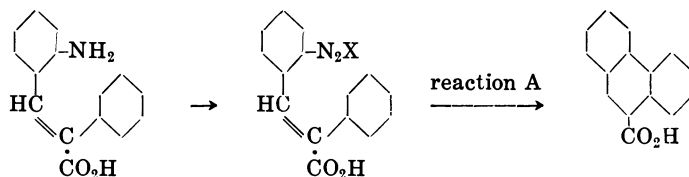
(6) Bell, *J. Chem. Soc.*, **1928**, 2773.

(7) *Ber.*, **39** (1906), 3061; **41** (1908), 3090 Anm.

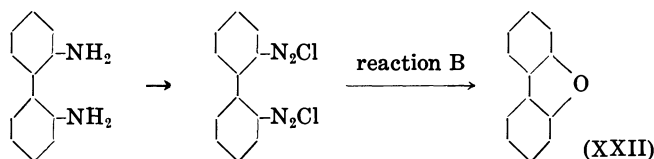
(8) Gabriel and Thieme, *Ber.*, **52** (1919), 1080.

yield, this work was made possible to proceed to further stages. At first, the problem of diazotizing 2-amino-3-nitrodiphenyl (XII) which had difficultly salt-forming property seemed a difficult one, but this could be surmounted by the use of conc. sulphuric acid in which the compound was diazotized smoothly.

It has already been stated that the tetrazonium salt derived from 2, 2'-diamino-6, 6'-diphenyl diphenyl (XVI) might decompose in three different ways. In the first place it will be remembered that there exists among compounds containing two benzene rings between which two carbon atoms are present and having in the ortho-position of one of the benzene rings a diazonium salt group a marked tendency with the loss of nitrogen to form a 6-membered ring resulting in the direct linking of the benzene rings. As an example for this may be cited the well-known synthesis of phenanthrene carboxylic acid by Pschorr's method⁽⁹⁾ from α -phenyl α -aminocinnamic acid (reaction A):



These conditions are as a matter of fact present on either side of the molecule of the tetrazonium salt obtainable from 2, 2'-diamino-6, 6'-diphenyl diphenyl (XVI). On the other hand, it will be recalled that when tetrazonium chloride solution prepared from 2, 2'-diaminodiphenyl, of which (XVI) is a derivative, was heated⁽¹⁰⁾ diphenylene oxide (XXII) was produced in a 70 per cent. yield (reaction B):

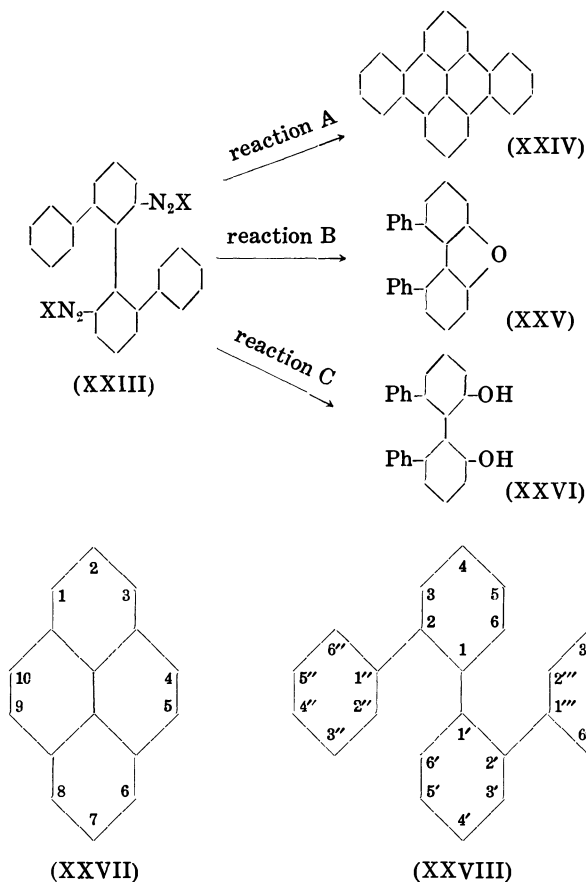


Finally, another possible decomposition of the tetrazonium salt is the production of the dihydroxyl compound without ring formation (reaction C). Thus in the decomposition of the tetrazonium salt (XXIII) obtained from 2, 2'-diamino-6, 6'-diphenyl diphenyl, according to whether reaction A,

(9) *Ber.*, **29** (1896), 496.

(10) Täuber and Halberstadt, *Ber.*, **25** (1892), 2745.

reaction B or reaction C occurs 4,5,9,10-dibenzopyrene (XXIV),⁽¹¹⁾ 4,5-diphenyl diphenylene oxide (XXV), or 2,2'-dihydroxy-6,6'-diphenyl diphenyl (XXVI) would result :



It would be reasonably supposed that the general principles stated in those views on the ease of formation of carbon rings⁽¹²⁾ can be applied equally to the formation of rings other than saturated. And if so, it may be stated at once that in the decomposition of the tetrazonium salt (XXIII) reaction A should take place more easily than reaction B, since, if the accepted formula for diphenyl is correct, the condition under which 4,5,9,10-dibenzopyrene (XXIV) is to be formed is perhaps one of the most favourable one

(11) The numbering for pyrene (XXVII) is one that was described in C., *Gen. Reg.*, VI (1922-1924), T. II, 816, for naming the then only known dibenzopyrene, 1,2,7,8,-dibenzopyrene, obtained by Scholl and Neumann (*Ber.*, 55 (1922), 123), who originally adopted another mode of numbering for pyrene.

(12) Sako, this Bulletin, 9 (1934), 41.

which can be imagined in ring formation ; in (XXVIII)⁽¹³⁾ the carbon atoms 6 and 2''' (or 6''') and 6' and 2'' (or 6'') can not but come close together when the four benzene nuclei are rotated around each common axis (Normally in the central diphenyl system which has two diazonium salt groups in the 6, 6'-positions only the semi-circular rotation is possible), and moreover no strain would be produced by the ring formation, a fact which implies that 4, 5, 9, 10-dibenzopyrene should be a stable substance as it is the case with pyrene, having the carbon atoms in one plane. In reaction B however there are at least two conditions which would be unfavourable to the production of the 5-membered ring in (XXV): one, the more important of the two, is the presence of the two phenyl groups in the 2, 2'-positions which should hinder the two diazonium salt groups in the 6, 6'-positions to approach each other and the other is the production of strain which has to be overcome in forming the 5-membered ring. As a matter of fact, this inference was fully borne out by the experiment.

It has been found that, although 4, 5, 9, 10-dibenzopyrene (XXIV) is produced by the decomposition of the tetrazonium salt (XXIII) even at ice-cold temperatures, 4, 5-diphenyl diphenylene oxide (XXV) can be obtained only when the decomposition is carried out at high temperatures. And whereas the yield of the dibenzopyrene (XXIV) is almost unchanged (36-40% of the theor.) whether the tetrazonium salt (XXIII) is decomposed in the cold or by heating, the yield of 4, 5-diphenyl diphenylene oxide (XXV) shows an increase with the rise of temperature at which the decomposition is effected (null below 45°C., 12 per cent. of the theor. at 60-70°C. and 30 per cent. at 100°C.).

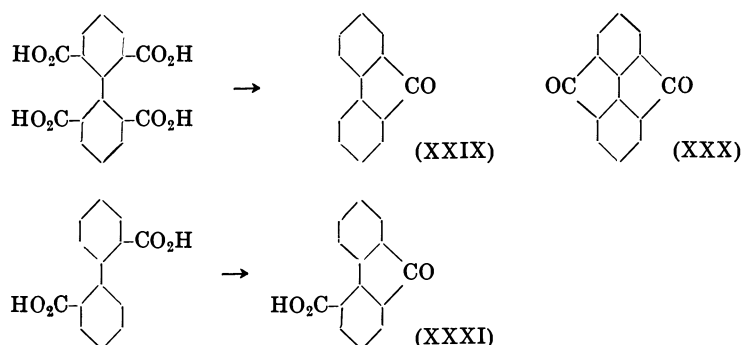
It is remarkable that neither the decomposition of the tetrazonium salt (XXIII) is at all promoted nor the yield of the dibenzopyrene (XXIV) is increased by the addition of copper powder to (XXIII), a phenomenon which is quite distinct from the production of phenanthrene carboxylic acid by Pschorr's method. As expected, 4, 5, 9, 10-dibenzopyrene is a very stable substance which melts without decomposition at 353-355°C. and can be distilled under reduced pressure.

The remarkable facility with which two six-membered rings in the dibenzopyrene (XXIV) are produced is in contrast with the repeated failure in attempting to produce two 5-membered rings, one on either side of the diphenyl molecule. Thus, fluorenone (XXIX) is produced in place of the substance (XXX) when diphenyl-2, 2', 6, 6'-tetracarboxylic acid is distilled,⁽¹⁴⁾

(13) For the ring system of 2, 2'-diphenyl diphenyl, the numbering shown by (XXVIII) is proposed.

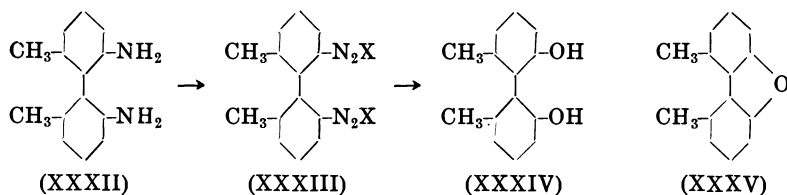
(14) Meyer, Meyer and Taeyer, *Ber.*, **53** (1920), 2034.

and the action of dehydrating agents on diphenic acid does not proceed beyond the stage of fluorenone carboxylic acid (XXXI):



This is probably due to the fact that by the formation of the 5-membered ring which may approximately be represented by a regular pentagon the distance between the carbon atoms in the 4,5-positions is increased so that the production of the other 5-membered ring is impossible. At the same time it suggests that the fluorenone molecule has probably a coplanar structure, since if it is possible to incline the plane of the benzene rings toward each other as in the manner of the Kaufler formula for diphenyl two five-membered rings should be formed without difficulty.

The view stated above that the non-production of the diphenyl diphenylene oxide (XXV) at low temperatures is due to the blocking effect of the two phenyl groups is supported by the fact that (1) diphenylene oxide (XXII) is produced by the decomposition of the tetrazonium salt obtained from 2,2'-diaminodiphenyl in which no such blocking group is present in nearly as good a yield at ordinary temperature (60% of the theor.) as at a high temperature (70%) and (2) the tetrazonium salt (XXXIII) derived from 2,2'-dimethyl-6,6'-diaminodiphenyl (XXXII) in which the methyl groups are the blocking groups on decomposition even with heating yields solely 2,2'-dimethyl-6,6'-dihydroxydiphenyl (XXXIV):

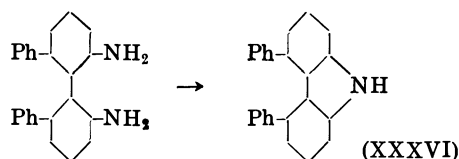


In the decomposition of the tetrazonium salt (XXXIII) reaction C apparently predominates over reaction B, no trace of the diphenylene oxide

derivative (XXXV) being produced even when the decomposition is effected by heating at 100°C . This is remarkable in view of the fact that, as already stated, 4,5-diphenyl diphenylene oxide (XXV) can be obtained in a 30 per cent. yield by heating the tetrazonium salt (XXIII) at the same temperature. This difference in behaviour between the two tetrazonium salts may be attributable to the fact that the tetrazonium salt (XXXIII) is very much less stable than (XXIII),⁽¹⁵⁾ since it is possible that when heating the cold solution of (XXXIII) its decomposition is completed before ever the temperature is reached which is necessary to enforce the production of the 5-membered ring against the blocking effect of the methyl groups. As a support for this view may be adduced the fact that, as already stated, whilst the yield of diphenylene oxide (XXII) from the tetrazotized solution of 2,2'-diaminodiphenyl in which no blocking group is present is not much influenced by the temperature at which the decomposition is effected, 4,5-diphenyl diphenylene oxide (XXV) is produced from the tetrazonium salt (XXIII) only at high temperatures, its yield being increased with the rise of temperature.

It has been found that reaction C occurs to a very slight extent when the tetrazonium salt (XXIII) is decomposed at 100°C ., the 2,2'-dihydroxy-6,6'-diphenyl diphenyl (XXVI) being obtained in about 5% of the theoretical. No trace of the latter (XXVI) could be detected in the product obtained by decomposing (XXIII) at lower temperatures. In the decomposition of the tetrazotized solution of 2,2'-diaminodiphenyl either in the cold or by heating reaction C does not occur at all, the product being solely diphenylene oxide (XXII) resulting from reaction B. The difference between the two cases may again be regarded as evidence demonstrating that the closure of the diphenylene oxide ring through the 2,2'-positions is hindered by the blocking effect of the large groups in the 6,6'-positions.

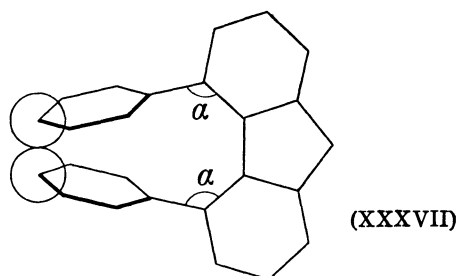
4,5-Diphenyl carbazol (XXXVI), the constitution of which is analogous to 4,5-diphenyl diphenylene oxide, has been obtained by heating 2,2'-diamino-6,6'-diphenyl diphenyl with hydrochloric acid :



The constitution of 4,5-diphenyl diphenylene oxide or 4,5-diphenyl carbazol is a singular one, for if it is assumed that the diphenylene oxide

(15) The decomposition of (XXXIII) is complete in two to three days at ordinary temperature, while (XXIII) requires about a month to complete the decomposition under similar conditions.

and carbazol molecule each has a uniplanar configuration which can be roughly represented by a regular pentagon bearing regular hexagons on two of its sides, then as is clear from the diagram (XXXVII), the phenyl groups can not occupy their normal positions. In this diagram (XXXVII), the atoms constituting the carbazol or the diphenylene oxide molecule proper are supposed to be lying in the plane of the paper. The most probable form which the molecules of the substances may assume, that is to say, the least strained spatial arrangement for the valencies carrying the phenyl groups would be one in which the phenyl residues lie in planes perpendicular to the plane in which the carbazol or diphenylene oxide molecule proper lies. This is illustrated in the diagram (XXXVII) in which the heavily printed lines indicate the sides of hexagons which are nearer to the reader. If it is assumed, as shown in (XXXVII), that the relative position of the phenyl



groups are to be altered only by the deflection of the angle α and that the p - and p' -carbon atoms of the phenyl groups are in contact with each other with the distance of $1.45 \text{ \AA}$ between the centres of the atoms, the angle α will be 125.1° , but as the p - and p' -carbon atoms are not in actual combination, actually the distance from the centre

to centre of the carbon atoms will be somewhat longer and consequently the angle α will be somewhat larger than this. At any rate, whatever arrangement the molecule may assume, it is certain that the phenyl groups can not rotate about the bonds in these circumstances.

Experimental.

(A) *Preparation and Nitration of 2-Acetamidodiphenyl.*

2-Aminodiphenyl. The preparation of 2-aminodiphenyl from 2-nitrodiphenyl has been described by Scarborough and Waters.⁽⁶⁾ In the following is described a method improved by the author by which this substance can be easily obtained in the theoretical yield.

To a solution prepared by passing dry hydrogen chloride into a mixture of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (880 gr.) and EtOH (1000 c.c.) was added drop by drop 2-nitrodiphenyl (200 gr.) obtained by the method of Bell, Kenyon and Robinson⁽¹⁶⁾

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in the course of one hour, HCl being led in all the time (The nitro-compound must not be added too rapidly, otherwise a violent reaction would ensue, which may be beyond control). Shortly after the addition of the nitrodiphenyl the double chloride commenced to separate as needles which was collected on the following day. The crystals thus obtained contained about 60 per cent. of the theoretical amount of 2-aminodiphenyl, the rest, 40%, being obtained from the filtrate. The crystals were then dissolved in water, treated with alkali and the base thus set free extracted with ether. The ethereal residue, on distillation under diminished pressure gave pure 2-aminodiphenyl which had b.p. $135^{\circ}\text{C}/5.5\text{ mm.}$ The filtrate from the double salt was concentrated in a basin on the water bath into half the original bulk, made alkaline, and the base thus separated purified as before.

2-Acetamidodiphenyl (X). For the acetylation of 2-aminodiphenyl Scarborough and Waters⁽¹⁵⁾ preferred acetyl chloride to acetic anhydride, the reason for this being, according to their statement, that the oily product obtained by heating the base with acetic acid or a mixture of acetic acid and acetic anhydride crystallized only with difficulty and with considerable loss. The author found however that the apparently poor yield of 2-acetamidodiphenyl when acetic anhydride was used was due to its extremely soluble property in acetic acid. The theoretical yield of the acetamidodiphenyl could therefore be obtained when the acid was removed. This was not the only instance observed by the author that such was the case. On more than one occasion it was found that the difficulty of crystallizing the products obtained by acetylating certain amines with acetic anhydride was due to the same cause.

Acetic anhydride (110 gr.) was added to a solution of 2-aminodiphenyl (176 gr.) in benzene (200 c.c.) at ordinary temperature. The reaction occurred at once, but it was allowed to stand until the next day to complete the separation of the crystals. 2-Acetamidodiphenyl thus obtained, 92 gr., formed needles melting at 120°C. The mother liquor containing the major part of the product was greatly diluted with benzene, shaken with a sodium carbonate solution and the benzene layer greatly concentrated. In this way 2-acetamidodiphenyl was obtained in the theoretical yield.

3-Nitro-2-acetamidodiphenyl (XI). As stated in the introduction 3- and 5-nitro-2-acetamidodiphenyl were produced by the mononitration of 2-acetamidodiphenyl in presence of acetic anhydride and acetic acid. As however the yield of the 3-nitro-compound was not good, the nitration was carried out under a great variety of conditions, but even under the best conditions thus arrived at the combined yield of the two nitration products amounted to only 50 per cent. of the theoretical, the rest being an uncrystal-

lizable syrup and tarry matter. It will be noticed in the experiment described below that the quantities of both nitric acid and acetic anhydride employed are about one and a half time the theoretical amount required for the mononitration, the reason for this being that when the theoretical quantities of these substances were used, 25 per cent. of the original compound remained unattacked. The use of more than the amount given in the direction led however to a lower yield of the desired substance.

2-Acetamidodiphenyl (42.2 gr.) was dissolved with heating in a mixture of acetic anhydride (30 c.c.) and glacial acetic acid (35 c.c.). The solution was agitated mechanically and cooled with water which was kept at about 22°C.

When the temperature of the liquid reached 23–24°C., the solution from which some crystals reappeared was treated with a solution of fuming nitric acid (20 gr.; $D = 1.5$) in glacial acetic acid (15 c.c.) in the manner described below. Two-fifths of the nitrating mixture was added during 20 minutes, when the reaction set in with a rise of temperature, the crystals gradually disappearing. After this stage was reached, the nitration mixture must be added more slowly so that the reaction mixture, which as stated above was cooled with water at 22°C., was maintained below 26.5°C. It should be added here that the nitration does not proceed at all should the temperature of the liquid fall below 20°C. Under the conditions described above, about 100 minutes were required for the addition of the nitrating mixture. After three additional hours' agitation, it was allowed to stand over night in an ice box. It was then poured on 600 gr. of ice water, shaken with 300 c.c. of benzene and the upper layer left in an ice box for some hours to complete the separation of 3-nitro-2-acetamidodiphenyl. The light-yellow needles were then collected and washed once with benzene. 3-Nitro-2-acetamidodiphenyl thus obtained, 9 gr., was practically pure. From the mother liquor which was shaken with a sodium carbonate solution and then concentrated into a small bulk, was obtained a further crop of the same crystals which, on crystallization once from benzene, gave 2.6 gr. of 3-nitro-2-acetamidodiphenyl which had the same purity as the main portion. The total yield of the 3-nitro-compound was therefore 11.6 gr. or 22.6% of the theoretical. It may be recrystallized easily from benzene, from which it separated as light-yellow needles melting at 188–188.5°C. (Found.: $N = 11.2$. $C_{14}H_{12}O_3N_2$ requires $N = 10.9\%$). Twenty c.c. of boiling benzene dissolve about 1 gr. of 3-nitro-2-acetamidodiphenyl.

The combined mother liquors separated from 3-nitro-2-acetamidodiphenyl, containing 5-nitro-2-acetamidodiphenyl produced simultaneously by the nitration, were used for the isolation of the latter substance as described below.

2-Amino-5-nitrodiphenyl. As stated in the introduction, this compound has been obtained by Bell.⁽⁶⁾ It was found that 5-nitro-2-acetamidodiphenyl contained in the filtrate separated from 3-nitro-2-acetamidodiphenyl did not crystallize even when the filtrate was greatly concentrated. The solvent was therefore removed and the dark residual gum was purified by distillation under reduced pressure. At first some decomposition was noticeable but it ceased after a time.

The first fraction, 2.0 gr., distilled below 200°C./6 mm., the main fraction, 29.3 gr., boiling at about 245°C./6 mm. The main fraction, being also an uncrystallizable syrup, was hydrolyzed by boiling under reflux with 20 per cent. hydrochloric acid solution (90 c.c.) in an oil bath for 3 hours. The oily product was extracted with benzene and the solution, after being washed with an alkaline solution, evaporated off. The residual syrup thus obtained, on distillation under diminished pressure, yielded a distillate, 21.3 gr., which for the most part had b.p. 220–225°C./6 mm. On crystallization of the distillate from ethyl alcohol (25 c.c.), 2-amino-5-nitrodiphenyl, 10.2 gr., separated in an almost pure condition. The mother liquor was once more evaporated into dryness and the residue divided by vacuum distillation into two fractions boiling below and above 200°C./6 mm. From the higher fraction was obtained by crystallization from ethyl alcohol 1 gr. of 2-amino-5-nitrodiphenyl, making the total yield to 25.7 per cent. of the theoretical. The pure 2-amino-5-nitrodiphenyl had m.p. 125°C. (Found: C = 67.0; H = 5.2; N = 13.1. $C_{12}H_{10}O_2N_2$ requires C = 67.3; H = 4.7; N = 13.1%).

On reduction this compound yielded the diamino-derivative which showed the characteristic reactions of *p*-phenylene diamine, a fact which prove the constitution of the parent substance.

2, 5-Diaminodiphenyl Dihydrochloride. A well-ground mixture of 2-amino-5-nitrodiphenyl (3.2 gr.) and $SnCl_2 \cdot 2H_2O$ (13.2 gr.) was treated with conc. HCl (25 c.c.). No change was observed at ordinary temperature, but on gentle heating the reaction started, which then proceeded to completion without further heating, the double chloride separating while still hot. After cooling, the crystals, 7.2 gr. were collected and the tin removed in the usual way. The filtrate from the tin sulphide was greatly concentrated and left to crystallize. 2, 5-Diaminodiphenyl dihydrochloride, 2.8 gr., was thus obtained as almost colourless plates. It was found that, during the concentration of the solution mentioned above, the solution was kept almost colourless and that, even if it became coloured, it could be restored colourless by passing hydrogen sulphide. For purification, the hydrochloride was dissolved in a small quantity of water and the solution thus obtained treated

with conc. HCl. The colourless plates thus precipitated were dried over soda lime (Found: HCl = 28.5. $C_{12}H_{12}N_2 \cdot 2HCl$ requires HCl = 28.4%). That the amino-groups in this substance are in the 2,5-positions was proved by the fact that a solution of the hydrochloride, on treatment with H_2S and then with $FeCl_3$ solution, gave a deep violet precipitate.

2-Amino-3-nitrodiphenyl (XII). A hot solution of 3-nitro-2-acetamidodiphenyl (13 gr.) in ethyl alcohol (240 c.c.) was treated with conc. HCl (60 c.c.) and heated under reflux on the water bath for 5 hours. The greater part of alcohol was then removed by heating without reflux and water added. The oil thus separated was extracted with ether and the ethereal residue distilled under reduced pressure. The reddish oil thus obtained, 9.5 gr., boiling at $194-196^\circ C./6$ mm., became crystalline after a time. It melted at $44-45^\circ C$. The real m.p. might have been somewhat higher than this, but as no suitable solvent was found from which it could be crystallized, the matter was not further pursued. The analysis of the distillate gave the following result: Found, C = 67.7; H = 5.3. $C_{12}H_{10}O_2N_2$ requires C = 67.3; H = 4.4%.

2,3-Diaminodiphenyl Dihydrochloride. A well-ground mixture of 2-amino-3-nitrodiphenyl (2 gr.) and $SnCl_2 \cdot 2H_2O$ (8 gr.) was heated with conc. HCl (25 c.c.) on the water bath for some hours until the disappearance of the original substance. After allowing to stand for the night, the double salt was filtered off and dried over soda lime in a vacuum. It was then dissolved in water, treated with H_2S and the clear filtrate concentrated until its bulk was 7-8 c.c. On addition of conc. HCl (15 c.c.), the hydrochloride of the diamino-compound separated quickly in somewhat brown needles. For purification, its solution was treated with animal charcoal and the substance reprecipitated by conc. HCl.

Like most of the orthodiamines the substance was not stable, the chlorine determination of the hydrochloride giving a figure much lower than that required by theory. But the properties and the behaviour of the substance left no doubt whatever as to its being an ortho-diamine. Thus, an aqueous solution of the hydrochloride, on treatment with ferric chloride, yielded the red precipitate of the diaminophenazine derivative, a reaction which is characteristic of orthodiamines. Further, the most convincing evidence was afforded by the formation of the quinoxaline compound by the action of phenanthrene quinone on the hydrochloride as described below.

2,3-(*oo'*-Diphenylene)-5-phenyl Quinoxaline (XXI). Crystalline potassium acetate (0.6 gr.) was added to a warm solution of 2,3-diaminodi-

phenyl hydrochloride (0.77 gr.) in ethyl alcohol (10 c.c.). After cooling, the precipitated potassium chloride was filtered off and the filtrate added to a boiling solution of phenanthrene quinone (0.55 gr.) in glacial acetic acid (100 c.c.), when the quinoxaline derivative separated in yellow needles. Heating was continued for an hour and the crystal was collected after cooling. It melted sharply at 221°C. (Found: N = 8.1. $C_{26}H_{16}N_2$ requires N = 7.9%). The yield was 0.9 gr. or 95.6 per cent. of the theoretical, calculated on the phenanthrene quinone employed.

(B) *Preparation of 2,2'-Diamino-6,6'-diphenyl Diphenyl and its Conversion into 4,5-Diphenyl Carbazol.*

3-Nitro-2-iododiphenyl (XIV). A suspension of 2-amino-3-nitrodiphenyl (21.4 gr.) in conc. H_2SO_4 (100 c.c.) was agitated at ordinary temperature for about one hour, that is, until a clear solution was obtained. It was then cooled with ice water and treated with ice (50 gr.) and solid sodium nitrite (7.5 gr.) with vigorous stirring which was continued for one hour. Twenty grams of ice were then added and agitation continued for 40 minutes. The addition of a further quantity (20 gr.) of ice was followed after a short time by the production of a thick foam. When this foam disappeared, a large quantity of ice was added and the solution filtered to remove a trace of insoluble matter and then treated with a solution of potassium iodide (20 gr.). A vigorous decomposition occurred, the iodo-compound separating as an oil which at once crystallized. The crude compound, 32.5 gr., was dissolved in ether, shaken with a potassium hydroxide solution, and the ether removed. The ethereal residue on distillation in a vacuum gave the 3-nitro-2-iododiphenyl (30 gr.) in a state of purity. It had b.p. 178°C/4 mm. Recrystallized from ethyl alcohol it formed yellow needles which melted at 90–91°C. (Found: I = 38.73. $C_{12}H_8O_2NI$ requires I = 39.05%).

2,2'-Dinitro-6,6'-diphenyl Diphenyl (XV). The copper powder (20 gr.) prepared by the method of Piccard and Larsen⁽¹⁷⁾ was added within 7 minutes with vigorous agitation to 3-nitro-2-iododiphenyl (26 gr.) which was heated in an oil bath at 210–215°C, the heating being continued for 5 additional minutes. The mixture was extracted with benzene and the solution treated with animal charcoal. The crystalline residue from the benzene solution, 15.7 gr., was dissolved in boiling alcohol (800 c.c.) and the solution concentrated until half the original bulk. 2,2'-Dinitro-6,6'-diphenyl diphenyl separated on cooling as light-yellow crystals, 15 gr., melting at 201–

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202°C. The m.p. did not change with further crystallization (Found: N = 7.42. $C_{24}H_{16}O_4N_2$ requires N = 7.10%).

2, 2'-Diamino-6, 6'-diphenyl Diphenyl (XVI). A suspension of powdered 2, 2'-dinitro-6, 6'-diphenyl diphenyl (10 gr.) in a solution prepared by passing dry HCl to a mixture of stannous chloride (50 gr.) and glacial acetic acid (190 c.c.) was heated in a water bath at 50–60°C. with frequent shaking. The original substance disappeared in one hour but the heating was continued for 2.5 hours longer, hydrogen chloride being led in all the time. The solvent was then removed by distillation in a vacuum⁽¹⁸⁾ and the residue thus obtained, made alkaline and extracted with ether. The ethereal residue, 8.5 gr., quickly set to a mass of crystals, which on two crystallizations from alcohol gave almost colourless prisms, 6.5 gr., melting at 163–164°C. (Found: C = 85.5; H = 6.3. $C_{24}H_{20}N_2$ requires C = 85.7; H = 5.9%). The separation of the crystals from alcohol proceeded very slowly. The substance should be colourless when pure, but perfectly colourless crystals are difficult to obtain owing to oxidation. The hydrochloride as well as the sulphate of 2, 2'-diamino-6, 6'-diphenyl diphenyl are very difficultly soluble in water. Attempts to resolve the diamino-compound into optical isomers with *d*-tartaric, *d*-camphorsulphonic and *d*-bromocamphorsulphonic acids have been unsuccessful.

4, 5-Diphenyl Carbazol (XXXVI). 2, 2'-Diamino-6, 6'-diphenyl diphenyl (2 gr.) and 2n HCl (36 c.c.) were heated in a sealed tube in the atmosphere of carbon dioxide at about 200°C. for 7 hours. The brown mass thus obtained, on three crystallizations from ethyl alcohol, yielded colourless needles, 0.8 gr., which melted at 145–146°C. (Found: C = 90.0; H = 6.0; N = 4.4. $C_{24}H_{17}N$ requires C = 90.3; H = 5.3; N = 4.4%).

(C) *Decomposition of the Tetrazonium Sulphate (XXIII) obtained from 2, 2'-Diamino-6, 6'-diphenyl Diphenyl (XVI).*

The solution obtained by tetrazotizing 2, 2'-diamino-6, 6'-diphenyl diphenyl was decomposed under varied conditions: the decomposition was performed (i) at 100°C. in absence of copper powder, (ii) at 60–70°C. without the use of copper powder, (iii) at 40–45°C. in presence of copper powder and (iv) at ordinary temperature (5–15°C.) in absence of copper powder. It was found that 4, 5, 9, 10-dibenzopyrene (XXIV) was produced in each experiment with the yields varying from 36 to 40 per cent. of the theoretical, the other possible product, 4, 5-diphenyl diphenylene oxide (XXV) being

(18) The removal of the solvent must not be carried out under ordinary pressure, as in the case the product is darkened considerably by oxidation.

isolated only from the products obtained in (i) and (ii). 2,2'-Dihydroxy-6,6'-diphenyl diphenyl (XXVI) was found to be present only in the products obtained in (i). Possibly the latter (XXVI) might have been produced in the other experiments but its yield must have been very poor. The yields of the three substances obtained in the four experiments are tabulated below, the figures representing the percentages of the theoretical yields calculated on the 2,2'-diamino-6,6'-diphenyl diphenyl employed.

	(i)	(ii)	(iii)	(iv)
4, 5, 9, 10-dibenzopyrene	38%	40%	40%	36%
4, 5-diphenyl diphenylene oxide	30	12	0	0
2, 2'-dihydroxy-6, 6'-diphenyl diphenyl	5	0	0	0

The decomposition of the tetrazonium salt solution occurred even at ice-cold temperatures yielding the dibenzopyrene but the reaction velocity was very small. A feature in the decomposition of the tetrazonium salt was that the addition of copper powder to it had no effect to promote the decomposition as used to be the case in many diazonium salts. The only way to accelerate the reaction was to apply heating. The experiments were carried out as follows.

Experiment (i).—A suspension of powdered 2,2'-diamino-6,6'-diphenyl diphenyl (2.0 gr.) in a 15 per cent. sulphuric acid solution (25 gr.) was well agitated at 40–50°C. until completion of the salt formation. It was then cooled with ice water and treated with sodium nitrite (0.9 gr.). The very difficultly soluble sulphate of the base gradually disappeared forming after half an hour's agitation an almost clear solution. After filtration, the clear solution was poured into hot water in a beaker heated with boiling water bath. A short time later a vigorous decomposition took place yielding a dark gray precipitate which was collected and washed with water. The precipitate thus obtained, 1.9 gr. was found to contain the three substances, 4, 5, 9, 10-dibenzopyrene (0.66 gr.), 4, 5-diphenyl diphenylene oxide (0.55 gr.) and 2, 2'-dihydroxy-6, 6'-diphenyl diphenyl (0.05 gr.), which were separated as described on p. 72–73.

Experiment (ii).—The tetrazonium sulphate solution prepared from 2,2'-diamino-6,6'-diphenyl diphenyl in the same way as in the experiment (i) was heated without adding copper powder at 60–70°C. In this way 1.0 gr. of the diamino-compound gave 0.79 gr. of the precipitate from which 0.36 gr. of the dibenzopyrene (XXIV) and 0.12 gr. of 4, 5-diphenyl diphenylene oxide were obtained.

Experiment (iii).—The tetrazotized solution of 2,2'-diamino-6,6'-diphenyl diphenyl (1.0 gr.) was heated in presence of copper powder at 40–45°C. for two hours, at the end of which the reaction was complete.

The yield of the dibenzopyrene was 0.36 gr. Neither 4,5-diphenyl diphenylene oxide nor 2,2'-dihydroxy-6,6'-diphenyl diphenyl was produced.

Experiment (iv).—The tetrazonium sulphate solution obtained in the same way as before was allowed to decompose at room temperature (5–15°C.). The decomposition proceeded very slowly with separation of bluish green precipitate. From time to time a test portion was acted on an alkaline β -naphthol solution. It was thus found that no less than a month was required to complete the reaction. That the decomposition is very considerably hastened by heating will be seen from the fact that, as stated in the experiment (ii), it was completed at 40–45°C. in two hours. From 1 gr. of 2,2'-diamino-6,6'-diphenyl diphenyl, 0.32 gr. of 4,5,9,10-dibenzopyrene was obtained. As in the experiment (iii), 4,5-diphenyl diphenylene oxide and 2,2'-dihydroxy-6,6'-diphenyl diphenyl were not found among the products.

4, 5, 9, 10-Dibenzopyrene (XXIV). As described above, this compound was formed in the almost equal yields in the experiments (i), (ii), (iii) and (iv). In the following are described the method which was used for the separation of the three substances produced in the experiment (i).

An attempt was first made to extract the decomposition product (1.9 g., p. 71) obtained in the experiment (i) which contains the three substances (XXIV), (XXV) and (XXVI) with ethyl alcohol in which 4,5,9,10-dibenzopyrene (XXIV) alone is insoluble. But as the dibenzopyrene was in such a fine state that it passed freely through the filter the solvent was removed and the residue dissolved in boiling benzene (600 c.c.) and concentrated into a small bulk (60 c.c.). 4,5,9,10-Dibenzopyrene thus obtained, 0.66 gr., was, though somewhat brown, almost pure as was evidenced by the fact that it showed no change in appearance at 350°C. It was purified by distillation under reduced pressure (4 mm.) and then by crystallization from benzene. It formed lustrous minute crystals with faintly yellowish shade, which melted without decomposition sharply at 353–355°C. (Found: C = 95.3; H = 4.7. $C_{24}H_{14}$ requires C = 95.4; H = 4.6%). 4,5,9,10-Dibenzopyrene is insoluble or very difficultly soluble in usual organic solvents except boiling benzene in which it is slightly soluble. Thus in order to dissolve 1.0 gr. of the hydrocarbon, it must be boiled for a long time with 900–1000 c.c. of benzene.

The benzene filtrate separated from 4,5,9,10-dibenzopyrene which contained 4,5-diphenyl diphenylene oxide and 2,2'-dihydroxy-6,6'-diphenyl diphenyl was used for the isolation of these substances as described below.

4, 5-Diphenyl Diphenylene Oxide (XXV). The benzene solution separated from 4,5,9,10-dibenzopyrene as described above was evaporated off and the residue thus obtained extracted with ether. Some insoluble substance (0.06 gr.) was removed and the clear solution shaken with a dilute

potassium hydroxide solution. The alkaline layer was used for the isolation of 2, 2'-dihydroxy-6, 6'-diphenyl diphenyl as will be described later. The ethereal layer was then evaporated into dryness and the dark residue, 0.77 gr. crystallized from ethyl alcohol (50 c.c.). The crystals (0.45 gr.) thus obtained, though coloured dark, formed uniform needles melting at 150–153°C. and found to be fairly pure 4, 5-diphenyl diphenylene oxide. It was purified first by vacuum distillation and then by crystallization from ethyl alcohol. The colourless needles thus obtained melted at 154–155°C. (Found: C = 89.8; H = 5.5. $C_{24}H_{16}O$ requires C = 90.0; H = 5.0%). From the alcoholic mother liquors a further crop (0.10 gr.) of the 4, 5-diphenyl diphenylene oxide was obtained, making its total yield to about 0.55 gr. It is easily soluble in ether and fairly soluble in boiling ethyl alcohol but difficultly so in cold alcohol.

2, 2'-Dihydroxy-6, 6'-diphenyl Diphenyl (XXVI). This substance was contained in the alkaline layer separated from the ethereal layer containing 4, 5-diphenyl diphenylene oxide (see above). The alkaline solution on acidification precipitated this compound which was extracted with ether. As the ethereal residue was found to contain a trace of something which was insoluble in alkaline solution, it was treated with a warm aqueous potassium hydroxide solution and the insoluble matter filtered off. The filtrate was acidified, extracted with ether, and the ethereal residue recrystallized from petroleum ether (b.p. 60–70°C.). It formed colourless, slender needles melting at 145–147°C. The yield was 0.05 gr. The substance thus obtained was not quite pure (Found: C = 82.92; H = 5.85. $C_{24}H_{18}O_2$ requires C = 85.2; H = 5.3%), but there is no other alternative formula possible.

2, 2'-Dihydroxy-6, 6'-diphenyl diphenyl is easily soluble in ether, fairly soluble in ethyl alcohol and slightly soluble in boiling petroleum ether (b.p. 60–70°), but practically insoluble in cold petroleum ether.

(D) *Decomposition of the Tetrazonium Sulphates obtained from 2, 2'-Dimethyl-6, 6'-diaminodiphenyl and 2, 2'-Diaminodiphenyl.*

2, 2'-Dimethyl-6, 6'-dihydroxydiphenyl (XXXIV). This compound was obtained as the only isolable product when the tetrazotized solution of 2, 2'-dimethyl-6, 6'-diaminodiphenyl was decomposed. It was produced by effecting the decomposition either on heating or at ordinary temperature, but in the latter case its yield was only a trace.

A solution of 2, 2'-dimethyl-6, 6'-diaminodiphenyl, (4.24 gr.) in conc. sulphuric acid (12.0 gr.) and water (60 c.c.) was treated with sodium nitrite (2.9 gr.).

The tetrazonium sulphate solution was then poured into a beaker which was immersed in a boiling water bath. The decomposition was soon complete, a bluish dark precipitate being separated. The precipitate, 4.5 gr., was then submitted to steam distillation, a time-consuming work owing to the high b.p. of the product. The distillate was shaken with ether and the ethereal residue, about 1.5 gr., on crystallization from benzene (10 c.c.) gave 0.9 gr. of large colourless plates melting at 161–162.5°C. The m.p. was not altered by further crystallization (Found: C = 78.6; H = 7.0. $C_{14}H_{14}O_2$ requires C = 78.5; H = 6.5%).

2, 2'-Dimethyl-6, 6'-dihydroxydiphenyl is easily soluble in aqueous alkaline solution. It was found that, compared with the tetrazonium sulphates obtained from 2, 2'-diaminodiphenyl (see below) and 2, 2'-diamino-6, 6'-diphenyl diphenyl (see p. 72), the tetrazonium sulphate prepared from 2, 2'-dimethyl-6, 6'-diaminodiphenyl was very much less stable, its decomposition being completed at about 25°C. in two days or so.

Diphenylene Oxide (XXII). As stated in the introduction Täuber obtained this substance in a 70 per cent. yield by heating the tetrazonium salt solution made from 2, 2'-diaminodiphenyl. It was found that as described below the same compound was produced in a 60 per cent. yield by allowing the tetrazonium salt to decompose at ordinary temperature.

2, 2'-Diaminodiphenyl (3.68 gr.) dissolved in conc. H_2SO_4 (12.0 gr.) and water (60 c.c.) was treated with a solution of sodium nitrite (2.9 gr.) in water and the resulting tetrazonium salt solution left to decompose at ordinary temperature (about 25°C.), until a test portion of the liquid reacted no more with an alkaline β -naphthol solution. The reaction was complete in 24 days. The darkish precipitate was filtered off and the dried product, 3.1 gr., distilled under diminished pressure. The distillate (2.1 gr.) boiling at 120–125°C./5 mm. quickly set to a mass of crystals which, after being powdered, was extracted with an aqueous alkaline solution, by which treatment however no appreciable loss was observed in the weight of the distillate, a fact which indicates the absence in the distillate of the other possible product, 2, 2'-dihydroxydiphenyl. In order to be sure on this point, the alkaline solution was acidified, but no precipitation occurred. Furthermore, the acidified solution was shaken with ether and the ethereal layer evaporated off, but there was no residue. As a matter of fact, the distillate obtained above was almost pure diphenylene oxide. The crystals on crystallization from alcohol-water gave colourless crystals melting at 85–86°C.

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SOME CHEMICAL CHANGES OF MUSCLE PROTEINS IN CANNING.*

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Some changes take place in proteins and extractive matters of meats simply by heating in the case of canning. In this paper it is described on the study of the decomposition occurring in the muscle proteins.

The materials were prepared from muscles by removing substances soluble in water, alcohol and ether. The solutions of various pH values were added to the muscle proteins. The mixtures were sealed tightly in glass tubes and heated at 130-140°C. The purpose for adding the solutions of various pH values to the muscle proteins and heating them is to find out the changes of the muscle proteins in different hydrogen ion concentrations, and for using of glass-tubes is to learn the chemical changes free from the influence of any metallic can-materials.

(1) **Changes of the Hydrogen Ion Concentrations.** As the concentration of hydrogen ion of the contents of cans has great influences on etching the tin plated iron sheet of cans and on the chemical changes of the contents which occur during preservation, the experiments were carried out by the electric method for ascertaining the variation of pH value of muscle proteins by heating.

The proteins of whale, rabbit, hen, sea-bream, yellow-tail, carp, bonito, cuttle-fish and spiny-lobster were chosen as experimental materials. Either a slightly acidic or alkaline solution or distilled water was added to the proteins before heating. The results of experiments always showed the tendency of pH to approach towards the neutral value. For example, when the muscle proteins of whale were heated at the pH values of 3.4, 6.2 (adding water) and 8.5, the pH changed to 4.5, 6.6 and 8.1 respectively. Thus, it is considered that these variations were probably due to the volatile basic and acidic substances, such as ammonia and hydrogen sulphide, as well as to the soluble amphoteric electrolytes, such as polypeptide and amino acid produced while heating.

(2) **Changes of the Form of Nitrogen.** When the muscle proteins of whale, rabbit, cow, hen and mackerel were heated in distilled water at 150°C. for one hour, about 20 per cent. of their protein-nitrogen changed to

* This paper was already published more precisely in Japanese in Journal of the Society of Agricultural Chemistry of Japan, 9 (1933), 835.

the forms of peptone, peptide, amino acid and ammonia. The formation of these soluble nitrogenous substances may cause a speedy putrefaction to the opened canned meat. The distribution of nitrogen of the muscle proteins after heating is shown in Table 1.

Table 1.

	In per cent. of dry matter					In per cent. of total N			
	Total-N	Protein-N	Amino-N	Ammonia-N	Residual-N	Protein-N	Amino-N	Ammonia-N	Residual-N
Whale	16.35	13.52	0.52	0.09	2.22	82.69	3.18	0.55	13.58
Rabbit	15.88	11.35	0.78	0.02	3.73	71.47	4.91	0.13	23.48
Cow	16.52	14.31	0.43	0.29	1.49	86.62	2.60	1.76	9.00
Hen	16.86	13.90	0.52	0.31	2.13	82.44	3.08	1.83	12.63
Mackerel	16.81	14.18	0.45	0.34	1.84	84.35	2.68	2.04	10.95

(3) **Changes in the Elementary Composition of Muscle Proteins.** In order to ascertain what changes take place in the elementary composition of muscle proteins through heating under pressure, and to find out the effects of pH values upon these changes, the muscle proteins of whale, rabbit, hen and sea-bream were heated at the initial pH values of 3.4, 6.2 and 8.5. The results of experiments showed the decrease of their nitrogen and sulphur contents and the amounts of the decrease were particularly marked when the substances were heated in the solutions having the greater values of pH. The results are given in Table 2.

Table 2.

		C	H	N	S	P
Whale	Original protein	51.60	6.91	16.48	0.74	0.085
	Protein heated at pH 3.4	51.88	6.88	16.28	0.74	0.076
	pH 6.2	51.93	6.87	15.97	0.73	0.086
	pH 8.5	52.54	6.85	15.57	0.70	0.071
Rabbit	Original protein	52.32	7.12	16.30	0.86	0.093
	Protein heated at pH 3.4	52.47	7.13	16.11	0.86	0.078
	pH 6.2	52.55	7.11	15.92	0.83	0.092
	pH 8.5	52.99	7.05	15.38	0.84	0.069

Table 2.—(Concluded)

		C	H	N	S	P
Hen	Original protein	52.53	7.18	16.76	0.85	0.093
	Protein heated at pH 6.2	52.88	7.14	16.33	0.84	0.094
Sea-bream	Original protein	52.79	7.08	16.42	0.95	0.095
	Protein heated at pH 6.2	52.92	7.03	16.07	0.93	0.093

(4) **Generation of Ammonia and Hydrogen Sulphide.** The results of experiments with four kinds of muscle proteins revealed the fact that both NH_3 and H_2S were generated in larger quantities when they were heated in the solutions having the greater values of pH. This fact agrees with the result of the elementary analysis. When the material of the tin is bad and iron dissolves in the liquid contained in the can, then sulphide of iron precipitates and causes the deterioration and blackening of the canned meats. The amounts of NH_3 and H_2S in mg. generated from 100 gr. of muscle proteins are shown in Table 3.

Table 3.

NH_3 (mg. in 100 gr. of proteins)

pH before heated	Whale	Rabbit	Hen	Sea-bream
3.4	0.15	0.21	—	—
6.2	0.58	1.76	1.36	1.88
8.5	28.44	36.89	—	—

H_2S (mg. in 100 gr. of proteins)

pH before heated	Whale	Rabbit	Hen	Sea-bream
3.4	0	0	—	—
6.2	9.37	1.14	0.87	15.62
8.5	27.72	12.89	—	—

(5) **Changes of the Amounts of Arginine, Histidine, Lysine, Cystine, etc.** In order to learn how the distributions of arginine, histidine, lysine, cystine and other nitrogen in the muscle proteins of whale, rabbit, hen and sea-bream change by heating, the quantitative analyses were carried out by the Van Slyke method before and after the heating. The proteins were heated at three different values of pH to ascertain the effects of solutions of various pH upon the proteins. The results are as follows (Table 4).

Table 4.

Whale									
	Total-N	Ammono- nia-N	Mela- nine-N	Cystine- N	Argini- ne-N	Histi- dine-N	Lysine- N	Mono- amino-N	Non- amino-N
In per cent. of protein									
Original protein	16.48	0.69	0.33	0.29	2.49	2.20	1.34	8.02	1.18
Protein heated at pH 3.4	16.28	0.59	0.45	0.16	2.59	2.28	1.16	7.79	1.23
pH 6.2	15.97	0.55	0.44	0.14	2.36	2.36	1.26	7.66	1.21
pH 8.5	15.57	0.45	0.43	0.10	2.49	1.96	1.34	7.45	1.35
In per cent. of total N									
Original protein	100	4.29	2.02	1.45	15.08	13.37	8.15	48.66	7.15
Protein heated at pH 3.4	100	3.62	2.79	1.04	15.94	14.03	6.48	47.84	7.67
pH 6.2	100	3.42	2.73	0.87	14.77	14.79	7.88	47.95	7.57
pH 8.5	100	2.91	2.73	0.64	15.97	12.59	8.62	47.85	8.64
Rabbit									
In per cent. of protein									
Original protein	16.30	0.74	0.36	0.19	2.49	1.93	1.26	8.17	1.15
Protein heated at pH 3.4	16.11	0.73	0.46	0.15	2.58	1.92	0.94	7.82	1.41
pH 6.2	15.92	0.50	0.38	0.13	2.34	2.17	1.15	7.89	1.34
pH 8.5	15.38	0.39	0.43	0.10	2.49	1.75	1.23	7.59	1.41
In per cent. of total N									
Original protein	100	4.56	2.17	0.18	15.28	11.85	7.74	50.15	7.06
Protein heated at pH 3.4	100	4.55	2.83	0.92	16.04	12.53	6.04	48.45	8.78
pH 6.2	100	3.81	2.36	0.79	14.41	13.60	6.92	49.61	8.43
pH 8.5	100	2.57	2.77	0.65	16.16	11.38	8.02	49.32	9.18

Table 4.—(Concluded)

Hen									
	Total-N	Ammonia-N	Melanine-N	Cystine-N	Arginine-N	Histidine-N	Lysine-N	Mono-amino-N	Non-amino-N
In per cent. of protein									
Original protein	16.76	1.10	0.48	0.18	2.71	1.97	1.36	8.19	0.76
Protein heated at pH 6.2	16.33	0.89	0.63	0.14	2.55	2.04	1.15	7.97	0.97
In per cent. of total N									
Original protein	100	6.58	2.85	1.07	16.14	11.73	8.12	49.60	4.53
Protein heated at pH 6.2	100	5.42	3.88	0.85	15.61	12.51	7.04	48.78	5.95
Sea-bream									
In per cent. of protein									
Original protein	16.42	0.77	0.36	0.28	2.54	2.24	1.47	8.35	0.42
Protein heated at pH 6.2	16.07	0.45	0.48	0.12	2.46	2.36	1.37	8.20	0.51
In per cent. of total N									
Original protein	100	4.70	2.17	1.69	15.46	13.61	8.92	50.83	2.55
Protein heated at pH 6.2	100	3.43	2.99	0.77	14.68	14.71	7.93	50.42	3.17

It was found that the total nitrogen, ammonia and cystine nitrogen always decrease by heating, and the higher the value of pH the greater the rate of the decrease, while melanine nitrogen generally increases. The amounts of cystine, arginine, histidine and lysine contained in the proteins before and after heating were calculated in per cent. from the above results.

Table 5.

		Cystine	Arginine	Histidine	Lysine
Whale	Original protein	2.49	7.74	8.12	6.99
	Protein heated at pH 3.4	1.37	8.04	8.41	6.05
	pH 6.2	1.20	7.33	8.71	6.57
	pH 8.5	0.86	7.74	7.23	6.99
Rabbit	Original protein	1.63	7.74	7.11	6.57
	Protein heated at pH 3.4	1.29	8.02	7.09	4.90
	pH 6.2	1.11	7.27	8.01	6.00
	pH 8.5	0.86	7.74	6.46	6.41

Table 5.—(Concluded)

		Cystine	Arginine	Histidine	Lysine
Hen	Original protein	1.54	8.42	7.27	7.09
	Protein heated at pH 6.2	1.20	7.92	7.53	6.00
Sea-bream	Original protein	2.40	7.89	8.27	7.67
	Protein heated at pH 6.2	1.03	7.64	8.71	7.14

According to Table 5, the quantities of cystine, arginine, histidine and lysine contained in the proteins after heating showed a tendency of decrease, as compared with those contained in the original proteins. Such tendencies were remarkable on cystine at the higher pH before heating and on lysine at the lower pH.

(6) **Changes of Tyrosine and Tryptophane.** The quantities of tyrosine and tryptophane contained in the muscle proteins of whale, hen, rabbit, yellow-tail, carp, bonito, sea-bream, cuttle-fish and spinylobster were determined before and after heating. The amounts of those amino acids decreased by heating, but very little, as it is obvious in Table 6.

Table 6.

Proteins	Tyrosine		Tryptophane		pH	
	Before heating	After heating	Before heating	After heating	Before heating	After heating
Whale	5.11	4.97	1.51	1.32	6.2	6.6
Hen	4.81	4.78	1.58	1.59	6.2	6.6
Rabbit	5.49	5.27	1.68	1.57	6.2	6.6
Yellow-tail	4.97	4.69	1.70	1.62	6.51	6.54
Carp	4.71	4.53	1.50	1.47	5.02	5.92
Bonito	4.84	4.60	1.63	1.46	7.17	6.65
Sea-bream	5.00	4.74	1.63	1.56	6.37	6.51
Cuttle-fish	4.83	4.71	1.37	1.29	4.67	5.57
Spiny-lobster	5.05	4.81	1.46	1.34	3.98	5.29

(7) **Change of Proline.** The experiments were carried out by using each 40 gr. of gelatine to find out the difference between the quantities of

proline contained in the materials before and after heating. It was observed that there was almost no difference between them, and when the pure solution of proline was heated, there was no detectable decomposition. Therefore the amount of proline in muscle proteins may probably be the same.

(8) **Changes of the Forms of Cysteine, Cystine and Sulphur.** When the solutions of pure cystine and cysteine were heated under the different pH, a part of the one always changed into the other. That is, when the solution of any of the two acids was heated, it was found that the solution contained the both acids, but the sum of the two quantities always decreased. The results of the experiments are as follows :

Table 7.

pH, before heating	Sample	Used, mg.	Found, mg.		Sum
			Cysteine	Cystine	
1.7	Cysteine	37.5	32.0	3.8	35.8
4.8	Cystine	45.6	2.9	39.9	42.8
6.8	Cysteine	25.1	9.4	6.6	16.0
6.8	Cystine	22.6	2.7	17.1	19.8
8.3	Cysteine	25.8	5.1	5.3	10.4
8.6	Cystine	25.0	2.7	16.2	19.2

The muscle proteins of sea-bream were heated at pH 6.1 (a) and 9.2 (b), and the forms of sulphur were determined. The results obtained are as follows :

Table 8.

Mg. per cent. of protein	Total S	Cysteine	Cystine	H ₂ S S	Sulphide S	Sulphate S	Soluble- organic S
Before heating	690	660	190	—	—	—	—
After heating (a)	—	490	200	6.6	0.4	18	96
„ „ (b)	—	440	110	20.9	4.6	30	103

In per cent. of total S	Total S	Cysteine S	Cystine S	H ₂ S	Sulphide S	Sulphite S	Soluble- organic S	Protein S
Before heating	100	26.0	7.2	—	—	—	—	—
After heating (a)	—	19.0	7.5	0.9	0.06	2.6	14.0	82.4
„ „ (b)	—	17.5	4.3	2.9	0.7	4.3	15.0	77.1

Namely, when it was heated in alkaline solutions, the decompositions of cysteine and cystine were especially considerable, and hydrogen sulphide and other sulphides were formed in large quantities.

In conclusion the authors wish to express their thanks to Messrs. U. Endo, S. Nagatake, S. Shigematsu and K. Katai for their analytical works and also to "Hatutori-Hokokuwai" for a research grant which has defrayed a part of the cost of this investigation.

Summary.

(1) The muscle proteins of some hens, various fishes and certain animals were prepared as samples for the purpose of studying what changes take place in the muscle proteins at the time of canning meats under pressure and heating. The materials were sealed in glass-tubes and heated at 130–140°C. for one hour, and changes of materials were studied.

(2) The hydrogen ion concentration of all of the proteins showed a tendency to approach toward the neutral point.

(3) About 20 per cent. of the protein nitrogen was transformed by heating to peptone, peptide, and amino acid nitrogens. The formation of soluble nitrogen compounds, such as these, is considered to cause a speedy putrefaction of contents of an opened can.

(4) As the results of elementary analyses of carbon, hydrogen, nitrogen, sulphur and phosphorus, it was found that the quantities of nitrogen and sulphur contained in the proteins generally decreased by heating, and the changes were more marked the higher the values of pH. There was no appreciable change in phosphorus when the solution was neutral, but its amount decreased when the solution was acidic or alkaline, and hence the percentage of carbon increased.

(5) The quantities of NH_3 and H_2S generated by heating were greater in proportion to the values of pH of the solutions. This result explains the fact that, when the tin of cans are bad and the pH of the contents is high, the contents of the can deteriorate more readily and the colour changes to black.

(6) As the results of the analyses of the proteins by the Van Slyke method, the decrease of the total nitrogen, ammonia nitrogen and cystine nitrogen and the increase of melanine nitrogen were detected especially when the pH value increased. The quantities of cystine, arginine, histidine and lysine contained in the materials showed a tendency of decrease in all

three cases and the same tendencies were very remarkable on cystine at the higher value of pH and on lysine at the lower.

(7) Tryptophane by the May-Rose method and tyrosine by the Folin-Denis method were quantitatively analyzed, and the decreases of these substances by heating were very insignificant.

(8) The test for proline was made by the Fisher-Bechner method, but no decomposition by heating was observed.

(9) Cysteine and cystine were analyzed quantitatively by the Okuda-Katai method, and it was found that a part of any one of these acids always changed to the other acid by heating. But the sum of the two always decreased, and the decomposition of both of these acids was remarkable at the higher value of pH, and the decomposition of cysteine was greater than that of cystine.

(10) A part of the protein-sulphur changed by heating to hydrogen sulphide, other sulphides, sulphuric acid and soluble organic sulphur, and the quantities of these substances generated were greater at the higher pH of the solutions, as in the case of the decompositions of cysteine and cystine.

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GLUCOSULFATASE. IX.
ON THE SPECIFICITY OF THE ENZYME.

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The name "Glucosulfatase" has been provisionally given to our sulfatase because it seemed to hydrolyse most easily glucose-mono-sulphate. At that time the enzyme-solution had been prepared from *Eulota*, and had only a small activity, consequently the experimental result was somewhat obscure.⁽¹⁾ Meanwhile we have found in *Charonia lampas* a very suitable source of the enzyme⁽²⁾ and we know now that a very active enzyme can be obtained from its liver by a relatively simple method of purification.⁽³⁾⁽⁴⁾ Glucosulfatase has always been found together with phenosulfatase, but we

(1) This Bulletin, **6** (1931), 258.

(2) This Bulletin, **8** (1933), 65.

(3) *J. Chem. Soc. Japan*, **54** (1933), 377.

(4) This Bulletin, **8** (1933), 148.

have already pointed out the facts which prove that these two enzymes must be different with each other: that the former loses its activity in the alkaline medium while the latter does not,⁽⁴⁾ and that each has different tendency toward the adsorption of charcoal.⁽⁵⁾ Moreover we have recently succeeded to obtain a solution of glucosulfatase almost free from phenosulfatase.⁽⁶⁾ Therefore, it is now quite certain that our enzyme belongs to a new type of sulfatase. We do not know yet, however, whether the name "Glucosulfatase" has been properly adopted or not, for its specificity was tested only with a few substrates at the beginning of this work.⁽¹⁾

It would be now an urgent problem to settle the specificity of our enzyme and to give it an appropriate name. For this purpose we prepared following aliphatic sulphuric acid esters and examined their hydrolysability by the enzyme: ethyl sulphate, mannite-tetra-sulphate, chondroitinsulphuric acid, glucose-6-mono-sulphate, α -methyl-glucoside-mono-sulphate, mono-acetoneglucose-6-mono-sulphate, diacetoneglucose-3-mono-sulphate, fructose-tri-sulphate, galactose-di-sulphate, galactose-tetra-sulphate, mannose-mono- and di-sulphate, sucrose-di-sulphate and the same inverted, maltose-mono-sulphate, starch-di-sulphate. Not many sulphuric acid esters of sugars are known at present and we have had to synthesize some of them for the first time in this laboratory. The chemical constitution of these esters are mostly unknown, so any theoretical deduction from this experiment will be reserved. Fortunately, however, glucose 6-mono-sulphate has been found, as ever, to be the most easily hydrolysable substrate of all. Therefore the name "Glucosulfatase" still seems to be adequate.

The experiments were carried out side by side with those described in the communications V⁽⁴⁾ and VII,⁽⁵⁾ so that enzyme solution were common to each other, and the experimental procedure was about the same as before. The reaction mixtures had following composition.

Substrate solution (with BaCl ₂)	25 c.c.
Enzyme solution	25 c.c.
Chloroform (as an antiseptic) and BaCO ₃ (as a buffer) were added.	

10 c.c. of the above mixture were pipetted out, filtered with charcoal and the clear filtrate was decomposed with HCl; H₂SO₄ thus set free was weighed as BaSO₄.

Exp. I. The final purification of enzyme was done with Al(OH)₃-gel (Communication V. Exp. B. III). Solutions of substrates were about in the same molar concentration as free acids (0.07 Mol.).

(5) *J. Chem. Soc. Japan*, **54** (1933), 1069.

(6) It will be reported in "Glucosulfatase X".

Exp. II. Enzyme solution was further purified with charcoal after the treatment with $\text{Al}(\text{OH})_3$ -gel (Communication V. Exp. B. IV).

Exp. III. The enzyme solution was prepared according to the direction given in the communication VII, i.e. *dil.* NH_4OH is added to the crude autolysate from dried liver of *Charonia* and subsequently treated with Na_2SO_4 and BaCl_2 solution, pH being kept at 9.5–10.0. By such a treatment most of the phosphate which seems to inhibit the action of glucosulfatase, was precipitated and the activity of the enzyme increased. Further treatment was the same as Exp. II.

Results of the experiments are tabulated below.

Exp. I.

Substrate	BaSO ₄ mg.			% of hydrolysis	
	Initial	2 days	10 days	2 days	10 days
Glucose-SO ₃ -Ba	83.2	27.6	25.4	66.8	69.5
Galactose-(SO ₃) ₂ -Ba	139.6	109.2	81.6	21.8	41.6
Galactose-(SO ₃) ₄ -Ba	291.2	224.3	211.8	23.0	27.3
Sucrose-(SO ₃) ₂ -Na (inverted)	87.8	57.3	52.4	34.8	40.3

Exp. II.

Substrate	BaSO ₄ mg.		% of hydrolysis
	Initial	2 days	
Glucose-SO ₃ -Na	99.5	20.9	79.1
α -Methylglucoside-SO ₃ -Ba	94.6	45.9	56.5
Sucrose-(SO ₃) ₂ -Ba (inverted)	82.6	49.4	40.1
Galactose-(SO ₃) ₄ -Ba	78.4	58.2	38.5
Maltose-SO ₃ -Ba	93.7	61.1	34.8
Sucrose-(SO ₃) ₂ -Ba	76.5	69.2 (3 days)	9.5
Diacetoneglucose-SO ₃ -Ba	108.5	100.2	7.6
Mannite-(SO ₃) ₄ -Ba	100.1	98.7	1.4
Chondroitinsulphuric acid (Na)	121.0	120.6	0.3
Monoacetoneglucose-SO ₃ -Ba	80.1	80.0	0.0
Fructose-(SO ₃) ₃ -K	96.5	96.5	0.0
Ethyl-SO ₃ -Ba	149.3	149.5	0.0

Exp. III.

Substrate	BaSO ₄ mg.		% of hydrolysis
	Initial	2 days	
Glucose-SO ₃ -Ba	113.4	9.1 (1 day)	92.0
Mannose-SO ₃ -Ba	200.8	60.9	69.7
Sucrose-(SO ₃) ₂ -Ba	108.3	91.8	15.2
Starch-(SO ₃) ₂ -K ⁽⁷⁾	(221.5)	—	1.0

The preparation of substrates.

- (1) Glucose-6-mono-sulphate : Soda, this Bulletin, 8 (1933), 37.
- (2) Galactose-tetra-sulphate : Akamatsu, *Biochem. Z.*, 142 (1923), 181.
- (3) Diacetone-3-mono-sulphate : Ohle, *Biochem. Z.*, 136 (1923), 428.
- (4) Monoacetone-6-mono-sulphate : *ibid.*
- (5) Chondroitinsulphuric acid : Jorpes, *Biochem. Z.*, 204 (1929), 354. (prepared from cartilage).
- (6) Starch-di-sulphate : Tamba, *Biochem. Z.*, 141 (1923), 274.
- (7) Mannite-tetra-sulphate : Favre, *Ann. chim. phys.* (3) 11 (1844), 77. Favre had obtained di-ester, but in my case the product was found to be tetra-ester notwithstanding the same direction was followed. 3.6 Gr. of Ba-salt was obtained from 21 gr. mannite ; Ba-content : 34.8%, calculated for C₆H₈O₆(SO₃)₄Ba₂ : 35.25%.
- (8) Sucrose-di-sulphate : Soda, this Bulletin, 9 (1934), 1.
- (9) Sucrose-di-sulphate (inverted) ; The solution of the free acid of (7) was kept for few days at room temperature and then neutralized with BaCO₃. By such a treatment the disaccharide is splitted into a mixture of hexose-sulphate.
- (10) α -Methylglucoside-mono-sulphate : The same direction as (1) was applied to α -methylglucoside, but without fermentation with yeast. Yield : 8 gr. as Ba-salt from 20 gr. of glucoside. Content of Ba : 18.45%, calculated from (C₆H₁₀O₆CH₃SO₃)₂Ba·C₂H₅OH : 18.7%.
- (11) Galactose-di-sulphate : Galactose was, as glucose, treated in pyridin with chlorosulphonic acid. Its crude Ba-salt was purified by crystallizing it as brucine-salt, because the residual galactose could not be fermented off by the ordinary baker's yeast. From 15 gr. galactose 16 gr.

(7) As this substrate is precipitated by Ba-ion, the hydrolysed H₂SO₄ was estimated by alkalimetry (instead of BaCO₃ Na-acetate was used as a buffer pH : 5.4).

crude Ba-salt, and from the latter 6 gr. crystalline brucine-salt were obtained. Sulphur content of brucine salt: 5.65%; calculated from $C_6H_{10}O_6(SO_3\text{-brucine})_2$: 5.67%. $[\alpha]_{5461} = -8.3^\circ$ -10.1° ($c = 2.11$ in 10% alcohol). Ba-salt used for the experiment was prepared from this brucine salt. Galactose-meno-sulphate could not be obtained.

(12) Maltose-mono-sulphate: 20 gr. maltose dissolved in pyridin was sulphonated with chlorosulphonic acid and by exactly the same treatment as in the case of glucose its Ba-salt was prepared. Yield: 7 gr. The content of Ba: 12.5%; calculated from $(C_{12}H_{21}O_{11}SO_3)_2Ba \cdot C_2H_5OH$: 12.8%. $[\alpha]_{5461} = +97.0^\circ$ ($c = 3.36$). Its reducing power was increased about 1.44 times by heating its acidic solution at $100^\circ C$. for 4 hours (estimated by Hagedorn-Jensen-Hanes' method).

(13) Mannose-mono- and di-sulphate: The method of preparation was exactly the same as glucose-mono-sulphate. Ba-content of its Ba-salt was found to be 22.6% while the calculated value from $(C_6H_{11}O_6SO_3)_2Ba$ is 20.97%. Yield: 20 gr. 10 Gr. of the Ba-salt was changed into brucine-salt by usual way. Relatively insoluble salt of di-ester first crystallized out of its water-solution (about 1.6 gr.), and mono-ester, in the mother-liquor, crystallized out (15 gr.) when acetone was added in the hot solution. Analysis: Brucine-mannose-mono-ester $C_6H_{11}O_6SO_3H \cdot C_{23}H_{26}N_2O_4 \cdot H_2O$, found: 4.80% S; calculated 4.82%. $[\alpha]_{5461} = -14.26^\circ$ ($c = 1.825$). Brucine-mannose-di-sulphate $C_6H_{10}O_6(SO_3H \cdot C_{23}H_{26}N_2O_4)_2$, found: 5.65% S; calculated: 5.67%.

(14) Fructose-tri-sulphate: Dried fructose (18 gr.) was dissolved in pyridin (20 c.c.) and mixed with an alcoholic solution of pyridin-sulphonic acid (20 gr. in 50 c.c.). Then the mixture was evaporated to syrup at $60\text{--}70^\circ C$. under reduced pressure and kept at $35^\circ C$. for 2 days. Again it was evaporated under the same condition until no more bubbles could be seen; then it was dissolved in cold water and treated with barium hydroxide until it became just a little alkaline. The excess of $Ba(OH)_2$ was precipitated with CO_2 and the solution was evaporated at $40^\circ C$. under reduced pressure until free from pyridin. A little excess of H_2SO_4 was added to it and by treating with PbO and subsequently by passing H_2S the free acid of the acid-ester was obtained as its aqueous solution. It was neutralized with KOH and fermented over night with yeast to remove free sugar. It was filtered, concentrated under reduced pressure and precipitated by adding about its 10 volumes of absolute alcohol. Yield was about 10 gr. According to the analysis of this K-salt the percentage of K was found to be 21.95% and 21.86%, and that of S 17.67% and 17.93%; whereas percentages calculated from the formula $C_6H_9O_6(SO_3K)_3$ are found to be $K = 21.95\%$ and $S = 17.99\%$. $[\alpha]_{5461} = -5.4^\circ$ ($c = 3.03$).

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STUDIES OF THE RAMAN EFFECT. PART II. THE RAMAN
EFFECT OF PHENYL-ACETATES, PHENYL-PROPIONATE,
CINNAMATES, PHTHALATES, SALICYLATES
AND PHENYLMETHYLCARBINOL.

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Introduction.

The Raman effects of a series of esters of benzoic acid and phenol esters of fatty acids have been recently studied.⁽¹⁾ In order to confirm the constitutive influences exerted on the frequencies attributable to the benzene ring, between mono- and diderivatives, and to study the influences exerted on the -C=O linkage and the valency frequencies, of the $\text{-}\overset{\parallel}{\text{C}}\text{-O-R}$ system, the Raman spectra of the following nine kinds of alkyl esters of aromatic acids, viz., methyl phenyl acetate, ethyl phenyl acetate, ethyl phenyl propionate, ethyl cinnamate, iso-propyl cinnamate, dimethyl phthalate, diethyl phthalate, methyl salicylate and ethyl salycilate, and also for the comparison, methyl phenyl carbinol have been studied in the present investigation. Kohlrausch and Pongratz⁽²⁾ have shortly published the Raman spectra of dimethyl-phthalate and ethyl cinnamate. Their results are good agreement with ours, though the experimental data of ethyl cinnamate have not been thoroughly reported.

(1) This Bulletin, **8** (1933), 333.

(2) *Ber.*, (B) **66** (1933), 1-12.

Experimental.

The experiments were carried out with the same apparatus as described in our previous paper.⁽¹⁾ All the substances used were prepared in our laboratory by the following processes, excepting methyl salicylate.

Methyl and ethyl phenyl-acetates⁽³⁾ were made from the dehydrated alcohols and phenyl-acetic acid (made in Japan) by the action of conc. sulphuric acid.

Ethyl phenyl-propionate⁽⁴⁾ was prepared from dehydrated ethyl alcohol and phenyl-propionic acid which was obtained by reducing the cinnamic acid with sodium amalgam.

Ethyl and iso-propyl cinnamate⁽⁵⁾ were prepared from the corresponding alcohols and cinnamic acid (m.p. 133°C.), by the action of conc. sulphuric acid or dry hydrochloric acid gas.

Di-methyl and di-ethyl phthalates⁽⁶⁾ were prepared by boiling the corresponding absolute alcohols and phthalic acid in the presence of conc. sulphuric acid.

Ethyl salicylate⁽⁷⁾ was prepared from the absolute alcohol and the acid by the action of hydrochloric acid gas. As to methyl salicylate, Kahlbaum's was used.

Phenyl methyl carbinol⁽⁸⁾ was prepared from benzaldehyde by the action of magnesium methyl iodide, that is, the Grignard reagent.

For the simplification, the name of the substance, the number of the table (Tb. No.), the numbers of the Raman lines (n), the number of the plate (Pl. No.) and the conditions under which the spectra were taken, viz., breadth of the slit (St), electric current (C) working the mercury vapour lamp, temperature of the sample during the experiment (T) and the time of exposure (t), are tabulated.

(3) *Ber.*, **2** (1869), 208.

(4) *Ann.*, **137** (1866), 334.

(5) *Ber.*, **28** (1896), 3254.

(6) *Monat. Chem.*, **25** (1904), 1204.

(7) *Ann.*, **197** (1879), 17.

(8) *Ber.*, **31** (1898), 1003.

Table A.

No.	Substance	Tl. No.	n	Pl. No.	St. 10 ⁻² mm.	C (amp)	T° (C)	t (hours)
1	Methyl phenylacetate	I	42	{ 78	7	2.8	19	7
				{ 79	6	3.2	19	13
2	Ethyl phenylacetate	II	35	{ 80	7	3.2	20	8
				{ 86	6	3.2	20	13
3	Ethyl phenylpropionate	III	30	{ 92	7	3.2	20	13
				{ 94	6	3.2	20	15
4	Ethyl cinnamate	IV	72	{ 52	7	2.8	23	10
				{ 54	7	3.2	19	2
				{ 55	6	3.2	19	4
5	Isopropyl cinnamate	V	46	{ 105	6	2.8	21	4
				{ 106	6	3.2	21	3
6	Dimethyl phthalate	VI	37	{ 46	7	2.8	23	8
				{ 51	6	3.2	19	13
7	Diethyl phthalate	VII	42	{ 41	8	2.8	22	7
				{ 45	6	3.2	19	12
8	Methyl salicylate	VIII	34	{ 56	10	3.2	23	2
				{ 57	7	3.2	23	7
9	Ethyl salicylate	IX	35	{ 59	7	2.8	23	7
				{ 62	7	3.2	20	7
				{ 84	6	3.2	19	10
10	Methyl phenyl carbinol	X	41	{ 89	6	3.2	20	12
				{ 90	6	3.2	20	9

A small quantity (3-10 c.c.) of methyl-, ethyl phenyl-acetates, ethyl phenyl-propionate, iso-propyl cinnamate and methyl phenyl carbinol was used for each experiment. From the fact of the coincidence of most of the Raman lines in ethyl phenyl propionate and ethyl cinnamate, it is considered that the small quantity of the cinnamate may be mixed with ethyl phenyl propionate due to the insufficient reduction.

The strong back grounds in the plates of methyl-, ethyl- and phenyl-acetates and methyl- and ethyl salicylates could not be removed even when the pure samples obtained by the repeated purifications were examined. The data of the Raman spectra are tabulated as follows.

Table I.

Methyl phenyl acetate $C_6H_5 \cdot CH_2CO \cdot O \cdot CH_3$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24440	$\frac{1}{2}(b)$	q -2948	26	22169	$3(d)$	e - 769
2	24293	$\frac{1}{2}(b)$	p -3060	27	22120	$3(b, d)$	e - 818
3	24227	$1(b, d)$	k - 478	28	22047 ?	0	e - 891
4	24182	0	k - 523	29	22016 ?	$0(b)$	e - 922
5	24076	$\frac{1}{2}(bb)$	k - 629	30	21942	8	e - 996
6	24011	$1(b)$	k - 694	31	21913	3	e -1025
7	23952	$2(b)$	k - 753	32	21855	$1(d)$	e -1083
8	23894	$0(b, d)$	k - 811	33	21777	3	e -1161(k -2928)
9	23780	$1(d)$	k - 925	34	21754	$5(d)$	e -2951(e -1184)
10	23705	5	k -1000	35	21648	$7(b, d)$	k -3057
11	23681	2	k -1024	36	21562 ?	0	i -2954
12	23593	$2(b, d)$	k -1112	37	21502	$\frac{1}{2}(bb, dd)$	e -1436
13	23542	$0(b)$	k -1163	38	21338	$6(b, d)$	e -1600
14	23510	$2(b)$	k -1195(i -1006)	39	21196 ?	$2(bb, dd)$	e -1742
15	23434	$0(b)$	k -1271	40	20016	$\frac{1}{2}$	e -2922
16	23399 ?	$0(d)$	k -1306(i -1117)	41	19984	$3(b)$	e -2954
17	23311	$\frac{1}{2}$	i -1205	42	19881	2	e -3057
18	23274 ?	0	k -1431				
19	23103	2	k -1602				
20	22751	$3(d)$	e - 187				
21	22576	$\frac{1}{2}(b, d)$	e - 362				
22	22455	$3(b, d)$	e - 483				
23	22408	$\frac{1}{2}(d)$	e - 530				
24	22316	$3(b)$	e - 622				
25	22243	$\frac{1}{2}(d)$	e - 695				

$\Delta\nu$: 187 ($3d$); 362 ($\frac{1}{2}b, d$); 481 ($3b, d$); 527 ($\frac{1}{2}d$); 622 ($3b$); 695 ($\frac{1}{2}b, d$); 761 ($3d$); 818 ($3d$); 924 ($1d$); 998 (8); 1025 (3); 1083 ($1b$); 1112 ($3b, d$); 1162 ($3b$); (1189) ($5d$); (1271) ($\frac{1}{2}b, d$) ?; 1306 ($\frac{1}{2}b$); 1436 ($\frac{1}{2}bb, dd$); 1601 ($6b, d$); 1742 ($2b, d$); 2922 ($3b$); 2953 ($5d$); 3057 ($7b, d$).

Table II.

Ethyl phenyl acetate $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$.

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
1	24404	$1/2(d)$	q -2984	21	21969	$1/2$	f -1026
2	24302	$1/2$	p -3051	22	21944	8	e - 994
3	24238	$1(b)$	o -3055	23	21913	4	e -1025
4	24084	$2(b)$	k - 622	24	21823	$1(d)$	e -1115
5	23957	2	k - 749	25	21775	$5(dv)$	e -1163(k -2930)
6	23709	5	k - 996	26	21727	$5(b, d)$	e -1211
7	23683	3	k -1022	27	21623	$2(d)$	k -2978
8	23604	$2(d)$	k -1101	28	21650	$7(b, d)$	k -3055
9	23540	$2(d)$	k -1165	29	21543	$1/2(d)$	e -1395
10	23502	$3(d)$	k -1203	30	21483	$1(bb, dd)$	e -1455
11	23443 ?	$1/2$	k -1262	31	21338	$7(dv)$	e -1600
12	23312	$1/2$	k -1204	32	21201 ?	$1/2(dd)$	e -1737
13	23274	$1/2(b, d)$	k -1431	33	20016	$2(b)$	e -2922
14	23103	$1(d)$	k -1602	34	19953	$2(b)$	e -2985
15	22729 ?	$1/2(dd)$	e - 209	35	19884	2	e -3054
16	22316	3	e - 622				
17	22258		e - 680				
18	22180	$2(B)$	e - 758				
19	22150		e - 788				
20	22080	$2(B)$	e - 858				

$\bar{\Delta\nu}$: 209 ($1/2 dd$) ? ; 622 (3 b, d) ; 680 (2 b)—758 (2 b) ; 788 (2 b)—858 (2 b) ; 997 (8) ; 1025 (4) ; 1108 (1 d) ; 1164 (5 dv) ; 1207 (5 b, d) ; (1265) (2 d) ? ; 1395 ($1/2 d$) ; 1455 (1 bb, d) ; 1601 (7 dv) ; 1737 ($1/2 dd$) ? ; 2922 (2 b) ; 2981 (2 b) ; 3055 (7 b, d).

Table III.

Ethyl phenyl-propionate $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot CH_3$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	23885	$1/2(b)$	$k-820$	16	21945	7	$e-993$
2	23708	4	$k-997$	17	21915	$3(d)$	$e-1023$
3	23683	$1/2(d)$	$k-1023$	18	21833	$2(d)$	$e-1105$
4	23502	$4(b)$	$k-1203$	19	21791	6	$k-2914$
5	23443	$1/2(b, d)$	$k-1262$	20	21765	6	$e-1173$
6	23252	$1/2(d)$	$k-1453$	21	21742	6	$e-1196$
7	23213 ?	$1/2(d)$	$k-1495$	22	21681	$6(B)$	$e-1257(k-3024)$
8	23185	$2(d)$	$e+247$	23	21649		$k-3056$
9	23111	5	$k-1594$	24	21495	$2(b, d)$	$e-1443$
10	23076	5	$k-1629$	25	21447	0	$e-1491$
11	22766	$1(d)$	$e-178$	26	21343	8	$e-1595$
12	22701	$2(dr)$	$e-237$	27	21310	7	$e-1628$
13	22599	$1/2(d)$	$e-339$	28	21277	$1/2$	$e-1661$
14	22320	$2(b, d)$	$e-618$	29	21237	2	$e-1701$
15	22079	$1(b)$	$e-859$	30	19885	1	$e-3053$

$\Delta\nu$: 178 ($1d$); 237 ($2d$); 339 ($1/2d$); 618 ($2b, d$); 820 ($1/2b$) ?; 859 ($1b$); 995 (7); 1023 (2); 1105 ($2d$); 1173 (6); 1196 (6); 1257 ($5b$) ?; 1379 ($1/2$); 1448 ($2b, d$) ?; 1491 ($1/2$); 1595 (8); 1628 (7); 1661 ($1/2$); 1701 (2); 2914 (6); 2963 (6) ?; (3024) (5); 3055 ($5b$).

Table IV.

Ethyl cinnamate $C_6H_5 \cdot CH:CH \cdot CO \cdot O \cdot CH_2 \cdot CH_3$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24433 ?	$0(d)$	$k-272$	11	23709	6	$k-996$
2	24297 ?	0	$k-408$	12	23679	1	$k-1026$
3	24227	0	$k-478(i-289)$	13	23587	$1(d, b)$	$k-1118$
4	24119	$1(d, b)$	$i-397$	14	23549	$1(d)$	$i-967(k-1156)$
5	24088	2	$k-617$	15	23527	$8(d)$	$k-1178$
6	24047	1	$i-469$	16	23505	$8(d)$	$k-1200$
7	23989	$1(bb)$	$k-716$	17	23446	$6(d)$	$k-1259$
8	23869	2	$k-836$	18	23400	4	$k-1305(i-1110)$
9	23839	$2(d)$	$k-866$	19	23375	1	$k-1330$
10	23729	$1(d)$	$k-976$	20	23342	$3(d)$	$k-1363(i-1174)$

Table IV.—(Concluded)

No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
21	23315	3(<i>d</i>)	<i>k</i> -1390(<i>i</i> -1201)	51	21824	3(<i>b</i> , <i>d</i>)	<i>e</i> -1114
22	23258	5	<i>k</i> -1449	52	21782	3(<i>d</i>)	<i>k</i> -2923
23	23211	5	<i>k</i> -1494	53	21760	8(<i>s</i>)	<i>e</i> -1178
24	23172	2	<i>k</i> -1533(<i>i</i> -1339)(Hg)	54	21738	8(<i>s</i>)	<i>e</i> -1200(<i>k</i> -2980)
25	23154	$\frac{1}{2}$	<i>i</i> -1362	55	21679	6(<i>d</i>)	<i>e</i> -1259(<i>f</i> -1316)
26	23132	2	<i>k</i> -1573(<i>i</i> -1384)(Hg)	56	21638	5(<i>d</i>)	<i>e</i> -1300(<i>k</i> -3067)
27	23108	10	<i>k</i> -1597	57	21607	3	<i>e</i> -1331(<i>f</i> -1388)
28	23071	10	<i>k</i> -1634	58	21574	3	<i>e</i> -1364
29	23020	2	<i>i</i> -1496	59	21544	3	<i>e</i> -1994
30	22980	2	<i>i</i> -1536	60	21491	5	<i>e</i> -1447
31	22882	2	<i>i</i> -1634	61	21464	$\frac{1}{2}$	<i>f</i> -1531
32	22823	$\frac{1}{2}$ (<i>b</i> , <i>d</i>)	<i>f</i> - 172	62	21445	5	<i>e</i> -1493(<i>i</i> -3071)
33	22761	2(<i>b</i> , <i>d</i>)	<i>e</i> - 177	63	21400	3	<i>f</i> -1595(<i>e</i> -1538)
34	22708	$\frac{1}{2}$ (<i>d</i>)	<i>f</i> - 287(Hg)	64	21367	3	<i>e</i> -1571(<i>f</i> -1622)
35	22659	1(<i>b</i> , <i>d</i>)	<i>e</i> - 279	65	21341	10	<i>e</i> -1597
36	22591	$\frac{1}{2}$ (<i>d</i>)	<i>f</i> - 404	66	21305	10	<i>e</i> -1633
37	22540	2(<i>d</i>)	<i>e</i> - 398	67	21296	1	<i>e</i> -1669
38	22466	0(<i>d</i>)	<i>e</i> - 472	68	21232	8(<i>d</i>)	<i>e</i> -1706
39	22367	4	<i>e</i> - 571	69	20073	2	<i>f</i> -2922
40	22323	6(<i>s</i>)	<i>e</i> - 615	70	20008	3	<i>e</i> -2920(<i>f</i> -2987)
41	22221	4(<i>b</i> , <i>d</i>)	<i>e</i> - 717	71	19957	3	<i>e</i> -2981
42	22163	3	<i>e</i> - 775	72	19874	5(<i>dv</i>)	<i>e</i> -3064
43	22126	0	<i>f</i> - 869				
44	22103	5	<i>e</i> - 835				
45	22071	5(<i>dr</i>)	<i>e</i> - 867				
46	22028	$\frac{1}{2}$?	<i>f</i> - 967				
47	21961	1(<i>d</i>)	<i>e</i> - 977(<i>f</i> -1034)				
48	21942	10(<i>s</i>)	<i>e</i> - 996				
49	21913	3(<i>s</i>)	<i>e</i> -1025				
50	21778	$\frac{1}{2}$ (<i>d</i>)	<i>f</i> -1117				

$\overline{\Delta\nu}$: 177 (2 *b*, *d*) ?; 279 (2 *bd*) ?; 403 (2*d*); 475 (0) ?; 571 (4); 616 (6 *s*); 717 (4 *b*, *d*) ?; 836 (5); 867 (5 *d*); 977 (1 *d*); 996 (10 *s*); 1025 (3); 1116 (3 *b*, *d*); (1156) (3); 1178 (8); 1200 (8); 1259 (6 *d*); 1303 (5 *d*); 1331 (3); 1363 (3); 1392 (3); 1447 (5); 1494 (5); (1536) (3); 1572 (3); 1597 (10); 1634 (10); (1669) (1); 1706 (8 *d*); 2922 (3 *d*); 2981 (3); 3067 (5 *d*).

Table V.

Iso-propyl cinnamate $C_6H_5 \cdot CH:CH \cdot CO \cdot O \cdot CH(CH_3)_2$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24093	$\frac{1}{2}$	k - 612	26	21941	8	e - 997
2	23897	$\frac{1}{2}$	k - 808	27	21913	1(d)	e -1025
3	23710	4(b)	k - 995	28	21883	1(d)	k -2822
4	23681	1	k -1024	29	21825	1	e -1113(k -2880)
5	23592	$\frac{1}{2}(\mathbf{d})$	k -1113	30	21778	1	k -2927
6	23526	6(d)	k -1179	31	21761	7	e -1177
7	23505	6	k -1200	32	21739	7	e -1201
8	23445	4(b)	k -1260	33	21672	5(d)	e -1266
9	23401	$\frac{1}{2}$	k -1304(i -1115)	34	21632	4(d)	e -1305
10	23318	1	k -1387(i -1198)	35	21543	$\frac{1}{2}$	e -1395
11	23254	1	k -1451(i -1262)	36	21489	4	e -1449
12	23209	1	k -1496	37	21446	4	e -1492(i -3070)
13	23107	8	k -1598	38	21398	2	f -1597
14	23072	8	k -1633	39	21367	3	e -1571
15	22755	1(bb)	e - 183	40	21343	9	e -1595
16	22399	$\frac{1}{2}$	e - 399	41	21306	10	e -1631
17	22463	0	e - 475	42	21231	8	e -1707
18	22369	1(d)	e - 569	43	21116	1	e -2822
19	22322	4	e - 616	44	20016	1(d)	e -2922
20	22257	1	e - 681	45	19962	$\frac{1}{2}(\mathbf{d})$	e -2976
21	22211	2	e - 727	46	19872	1(d)	e -3066
22	22168	1	e - 770				
23	22122	5	e - 816				
24	22077	5	e - 861				
25	22047 ?	$\frac{1}{2}$	e - 891				

$\overline{\Delta\nu}$: 183 (1 bb); 399 ($\frac{1}{2}$); 475 (0); 569 (1 d); 616 (4); 681 (1); 727 (2); 770 (1); 814 (5); 861 (5); 891 ($\frac{1}{2}$); 996 (8); 1025 (2); 1113 (1); 1177 (7); 1201 (7); 1266 (5 d); 1305 (4 d); 1391 ($\frac{1}{2} d$); 1450 (4); 1494 (4); 1597 (9); 1632 (10); 1707 (8); 2822 (1); 2925 (1 d); 2971 ($\frac{1}{2} d$); 3070 (4 d).

Table VI.

Dimethyl phthalate $C_6H_4 \cdot (CO \cdot O \cdot CH_3)_2$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24435	$1/2$	q -2953	21	22145	$1/2$	e - 793
2	24404	$1/2$	p -2949	22	21974	$2(b, d)$	e - 964
3	24319	$1/2$	q -3069(k - 386)	23	21899	6	e -1039
4	23885	2	k - 649	24	21856	$1(d)$	k -2849
5	23885	3	k - 820	25	21815	$3(d)$	e -1123
6	23741	$1(d)$	k - 964	26	21774	1	e -1163
7	23664	5	k -1041	27	21758	4	e -2947
8	23582	$1(b, d)$	k -1123	28	21666	$5(d)$	e -1272(i -2350)
9	23548	$2(d)$	k -1157(i - 968)	29	21633	$7(b, d)$	k -3072
10	23471	$1/2$	i -1045	30	21571	0	i -2945
11	23423	$4(b, d)$	k -1282	31	21492	1	e -1446
12	23265	$1/2(d) ?$	k -1440	32	21452	1	e -1486
13	23219	$1/2$	k -1486	33	21360	$1/2$	e -1578
14	23123	1	k -1582	34	21338	6	e -1600
15	23102	2	k -1603	35	21216	8	e -1722
16	22708	$1(d)$	e - 230	36	19988	4	e -2950
17	22641	0	e - 297	37	19868	3	e -3070
18	22539	$1(d)$	e - 399				
19	22287	$3(d)$	e - 651				
20	22120	6	e - 818				

$\overline{\Delta\nu}$: (230) ($1 d$) ?; 297 (0); 393 ($1 d$); 650 ($3 d$); 793 ($1/2$); 819 (6); 964 ($2 b, d$); 1040 (6); 1123 ($3 d$); 1160 (1); 1277 ($5 d$); 1443 (1); 1486 (1); 1580 (2); 1602 (6); 1722 (8); 2849 ($1 d$); 2947 (4); 3071 ($7 b, d$).

Table VII.

Diethyl phthalate $C_6H_4(CO \cdot O \cdot CH_2 \cdot CH_3)_2$.

No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in $cm.^{-1}$	I	$\nu_0 - \Delta\nu$
1	24416	$1/2$	q -2972	26	21836	4(d)	f -1159(k -2869)
2	24319	1(d)	q -3069	27	21816	2(d)	e -1122
3	24058	1(d)	k - 647	28	21779	7(b)	e -1159(k -2926)
4	23925 ?	0 ?	k - 780	29	21731	5(b)	k -2974(f -1264)
5	23860	1(b)	k - 845(i - 656)	30	21670	7(d)	k -1268
6	23670	5	k -1035(i - 846)	31	21632	8(b, d)	k -3073
7	23587	2(b, d)	k -1118	32	21577	2	e -1361(i -2939)
8	23544	2(b, d)	k -1161	33	21536	2	i -2978
9	23432	3(b, d)	k -1273	34	21489	3	e -1449
10	23334	$1/2$ (d)	k -1371	35	21449	2	e -1489(i -3067)
11	23252	2	k -1453(i -1253)	36	21367	2	e -1571
12	23220	$1/2$	k -1485	37	21342	9(s)	e -1596
13	23172	0	k -1532	38	21220	8(b)	e -1718
14	23128	3	k -1577	39	20065	1	f -2930(e -2873)
15	23107	5	k -1598	40	20009	2	e -2929
16	22807	4(b, d)	i -1709	41	19965	2	e -2973
17	22592	1(b, d)	e - 346	42	19867	3	e -3071
18	22545	2	e - 393				
19	22294	5(s)	e - 644				
20	22159	2(d)	e - 779(f - 836)				
21	22096	5	e - 842				
22	22015 ?	$1/2$	e - 923				
23	21982	$1/2$	f -1013				
24	21922	1	e -1016				
25	21904	8(s)	e -1034				

$\Delta\nu$: 346 (1 b, d); 393 (2); 644 (5 s); 779 (2 d); 843 (5); (923) ($1/2$); 1016 (1); 1034 (8 s); 1120 (2 d); 1160 (2 b); 1270 (7 d); 1362 (2); 1451 (3); 1487 (2); 1530 ($1/2$) ?; 1574 (3); 1597 (9 s); 1718 (8 b); 2871 (5 d); 2928 (4 b); 2974 (3 b); 3070 (8 b).

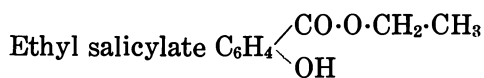
Table VIII.



No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0 - \Delta\nu$
1	24440 ?	$1/2$	k - 265	21	22134	6	e - 804
2	24282	1	k - 423	22	22093 ?	$1/2$	e - 845
3	24144	4	k - 561	23	21907	4	e -1031
4	23903	5	k - 802	24	21857	1	e -1081
5	23866	$1/2(b)$	k - 839	25	21808	3(d)	e -1130
6	23672	4	k -1033	26	21754	2	k -2951
7	23572	2(b, d)	k -1133	27	21695	5	e -1243
8	23460	5	k -1245	28	21614	5(dd, b)	k -3091(e -1324)
9	23377	5(b)	k -1328	29	21479	4(d)	e -1459
10	23270	$1/2$	i -1246	30	21364	$1/2$	e -1574
11	23240	3	k -1465	31	21335	1(d)	e -1603
12	23122	2(d)	k -1583	32	21266	5(b, d)	e -1672
13	23102 ?	$1/2(d)$	k -1603	33	19988	3	e -2950
14	22806 ?	1	f - 189	34	19861	3(b, d)	e -3077
15	22754	4	e - 184				
16	22677	$1/2(d)$	e - 261				
17	22582	2	e - 356				
18	22515	1	e - 423				
19	22424 ?	$1/2$	e - 514				
20	22380	4	e - 558				

$\overline{\Delta\nu}$: 184 (4); 264 ($1/2 d$) ?; (356) (2); 423 (1); (514) ($1/2$) ?; 560 (4); 804 (6); (845) ($1/2$) ?; 1032 (4); 1081 (1); 1132 (3 d); 1244 (5); 1326 (5 b, d); 1462 (4 d); 1578 (2 d); 1603 (1 d); 1672 (5 b, d); 2950 (3); 3084 (5 bb, dd).

Table IX.



No.	ν in cm^{-1}	I	$\nu_0 - \Delta\nu$	No.	ν in cm^{-1}	I	$\nu_0 - \Delta\nu$
1	24402	$1/2$	q -2986	21	21901	4	e -1037
2	24253	2	k - 453	22	21830	1	k -2875
3	24143	4	k - 562	23	21773	1(b)	k -2932
4	23898	4	k - 807	24	21727	1	k -2978
5	23856	3	k - 849	25	21696	6(b)	e -1242
6	23674	4	k -1031	26	21621	5(b, d)	k -3084(e -1031)
7	23364	$1/2(d)$?	k -1141	27	21575	$1/2$	e -1363
8	23462	5(b)	k -1243	28	21540	$1/2$	e -1398
9	23387	5(b)	k -1318	29	21479	4(d)	e -1459
10	23339	$1/2$?	k -1366	30	21327	$1/2(b, d)$?	f -1668
11	23312	$1/2$?	k -1393	31	21268	5(d)	e -1670
12	23238	4(b, d)	k -1467	32	20065	1(d)	e -2873
13	23119	1(b, d)	i -1396(k -1586)	33	20007	1(d)	e -2931(f -9288)
14	23102	1(b, d)	k -1603	34	19954	1(d)	e -2984
15	22771	3(b, d)	e - 167	35	19861	3(b, d)	e -3077
16	22693	2(d) ?	e - 245				
17	22481	$1/2(d)$	e - 457				
18	22381	4	e - 557				
19	22129	3	e - 809				
20	22090	2	e - 848				

$\overline{\Delta\nu}$: 167 (3 b, d); 245 ($1/2 d$) ?; 452 (2) ?; 559 (4); 808 (4); 848 (2); 1034 (4); 1141 ($1/2 b$); 1242 (6); 1318 (5 b, d); 1366 ($1/2$); 1395 ($1/2$); 1463 (4 b, d); (1586) (1 b, d) ?; 1605 ($1/2 b, d$) ?; 1670 (5 d); 2932 (1 d); 2980 (1 d); 3080 (5 b, d).

Table X.

Methyl phenyl carbinol $\text{C}_6\text{H}_5\cdot\text{CH}-\text{CH}_3$.
 OH

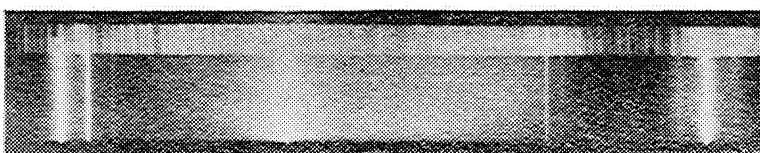
No.	ν in cm.^{-1}	I	$\nu_0-\Delta\nu$	No.	ν in cm.^{-1}	I	$\nu_0-\Delta\nu$
1	24219	$1/2$	k - 786	26	21865	$1/2(b, d)$	e -1073
2	23943	$1/2(d)$	k - 762	27	21835	$1/2(d)$	e -1103
3	23902	$1/2(d)$	i - 614	28	21783	$5(dr)$	k -2922(f -1212)
4	23711	5	k - 994	29	21740	7	e -1198(k -2965)
5	23684	2	k -1021	30	21674	1	e -1264
6	23500	$1/2(d)$	k -1205(i -1016)	31	21651	$8(b, d)$	k -3054
7	24437	$1/2(d)$	k -1268	32	21596	$0(d)$	i -2920
8	24311	0	k -1394(i -1205)	33	21543	1	e -1395(i -2973)
9	23257	$1/2$	k -1448	34	21494	$2(d)$	e -1444
10	23189	$2(d)$	k -1516(e - 251)	35	21458	3	i -3058
11	23108	$5(d)$	k -1597	36	21341	8	e -1597
12	22797	$5(b, d)$	e - 141	37	21261	$4(b, d)$	e -1678
13	22689	$2(b, d)$	e - 249	38	20081	1	f -2914
14	22619	$1(d)$	e - 319(f - 376)	39	20019	2	e -2919
15	22561	$0(b, d)$	e - 377	40	19964	$1/2(d)$	e -2974
16	22458	$1/2(d)$	e - 480(f - 531)	41	19886	$5(b)$	e -3052
17	22407	$1/2$	e - 531				
18	22324	4	e - 614				
19	22216	$1/2$	f - 779 ?				
20	22174	$4(b)$	e - 764				
21	22086	$1/2(d)$	e - 852 ?				
22	22039	$2(b)$	e - 899				
23	21980 ?	0	f -1015				
24	21947	10	e - 991				
25	21918	5	e -1020				

$\overline{\Delta\nu}$: 141 ($5b, d$); 249 ($2b, d$); (319) ($1d$) ?; (377) ($0d$) ?; 483 ($1/2$); (531) ($1/2$) ?; 614 (4); 763 ($4b$); 852 ($1/2d$); 899 ($2b$); 993 (10); 1021 ($1/2$); 1073 ($1/2b, d$); (1103) ($1/2d$); (1161) ($5d$) ?; 1201 (7); 1395 (1); 1446 ($2d$); 1597 (8); 1678 ($4b, d$); 2922 ($5dr$); 2971 (7) ?; 3054 ($8b, d$).

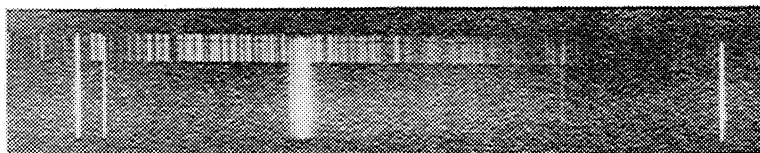
(1) Methyl phenyl acetate $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_3$



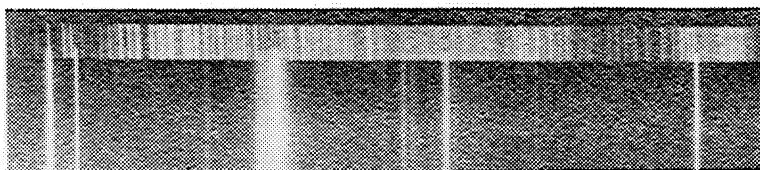
(2) Ethyl phenyl acetate $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_3$



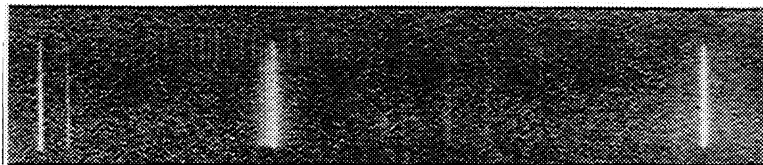
(3) Ethyl phenyl propionate $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_3$

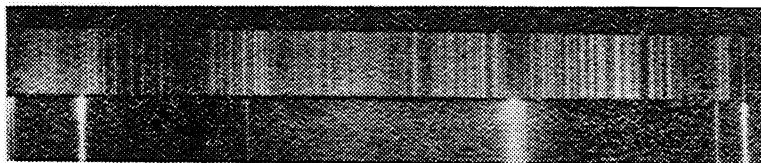
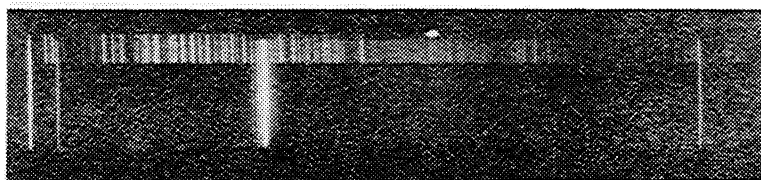
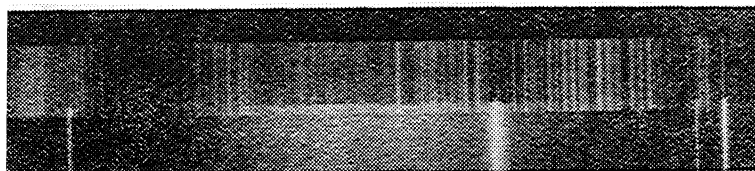
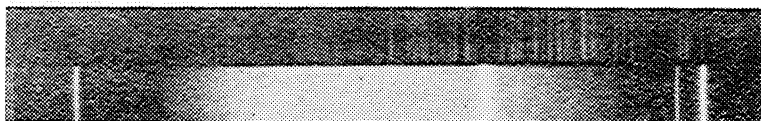
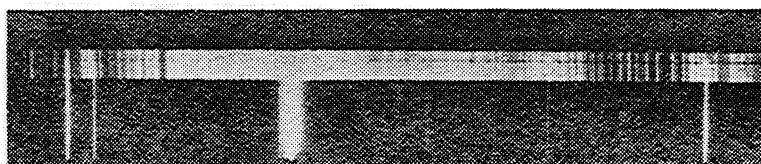


(4) Ethyl cinnamate $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_3$



(5) Iso-propyl cinnamate $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{CH}_3)_2$



(6) Di-methyl phthalate $\text{C}_6\text{H}_4\cdot(\text{CO}\cdot\text{O}\cdot\text{CH}_3)_2$ (7) Di-ethyl phthalate $\text{C}_6\text{H}_4\cdot(\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_3)_2$ (8) Methyl salicylate $\text{C}_6\text{H}_4\begin{matrix} \text{CO}\cdot\text{O}\cdot\text{CH}_3 \\ \text{OH} \end{matrix}$ (9) Ethyl salicylate $\text{C}_6\text{H}_4\begin{matrix} \text{CO}\cdot\text{O}\cdot\text{CH}_2\text{CH}_3 \\ \text{OH} \end{matrix}$ (10) Methyl phenyl carbinol $\text{C}_6\text{H}_5\cdot\text{CH}\begin{matrix} \text{CH}_3 \\ \text{OH} \end{matrix}$ 

Discussion of the Results. As reported in this and the previous paper,⁽¹⁾ the frequency of $\Delta\nu = 3060 \text{ cm.}^{-1}$ which has been known to be attributable to the C—H linkage in the benzene ring, was found as one of the most intense lines in the Raman spectra of the aromatic compounds investigated. For the comparison, the data observed are shown in the following :

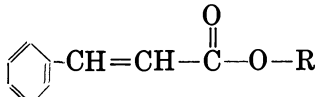
$\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{R} \dots\dots\dots$	3070 cm.^{-1}	$\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{Cl} \dots\dots\dots$	3067 cm.^{-1}
$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{R} \dots\dots\dots$	3057	$\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CO}\cdot\text{R} \dots\dots\dots$	3062
$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{R} \dots\dots\dots$	3056	$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{R} \dots\dots\dots$	3053
$\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{R} \dots\dots\dots$	3067	$\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{R} \dots\dots\dots$	3080
$\text{C}_6\text{H}_5\cdot\underset{\text{(OH)}}{\text{CH}}\cdot\text{CH}_3 \dots\dots\dots$	3054	$\text{C}_6\text{H}_4\cdot(\text{CO}\cdot\text{O}\cdot\text{R})_2 \dots\dots\dots$	3070

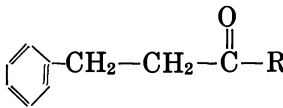
The results of other authors⁽⁹⁾ are ;

$\text{C}_5\text{H}_5\cdot\text{CH}_3 \dots\dots\dots$	3054 cm.^{-1}	$\text{C}_6\text{H}_5\cdot\text{CH}_2\text{NO}_2 \dots\dots\dots$	3059 cm.^{-1}
$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{Cl} \dots\dots\dots$	3054	$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2 \dots\dots\dots$	3057
$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{NH}_2 \dots\dots\dots$	3050	$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CBr}:\text{CH}_2 \dots\dots\dots$	3056
$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH} \dots\dots\dots$	3050	$\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_5 \dots\dots\dots$	3052
$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CN} \dots\dots\dots$	3057		

From these experimental data, we may suppose that in the aromatic compounds this frequency is influenced, to the first degree of approximation, only by the characteristics of the group or the atom adjacent to the carbon atom in the benzene ring.

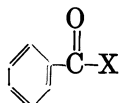
It is observed that the frequency in question is found to be $\Delta\nu = 3055 \text{ cm.}^{-1}$ in the compounds of  type, 3065 cm.^{-1} in those of  type and 3070 cm.^{-1} in those of  type. In the case of $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ ⁽⁹⁾ the shift is exceptionally small, i.e. is 3052 cm.^{-1} which may be due to its symmetric form.

The fact that the frequency in question is found to be 3067 cm.^{-1} in ethyl and iso-propyl cinnamates  and 3056 cm.^{-1}

in ethyl phenyl propionate  shows that the higher

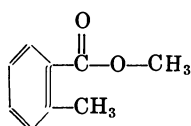
(9) Kohlrausch, "Der Smekal-Raman Effect," 328-332.

value of the frequency is due to the influence of the double bond of the

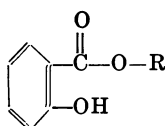
carbon, $-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-$, adjacent to the benzene ring, viz., .

Systematic studies⁽¹⁰⁾ of the derivatives of benzene have shown that the benzene nucleus is characterized by a number of very constant frequencies, viz., $\Delta\nu = 616, 1000, 1166$ and 1595 cm.^{-1} , and the aromatic C—H frequency of 3060 cm.^{-1} which has been just mentioned.

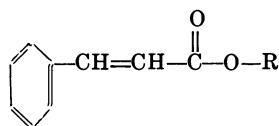
In the present experiment, it was observed that frequencies of $\Delta\nu = 615$ and 1000 cm.^{-1} were shown in a good constancy in monoderivatives of benzene and they disappeared in the case of di-derivatives such as phthalates, salicylates and *o*-kresyl acetates. In place of 615 cm.^{-1} in the di-derivatives (ortho), however, the frequency of $\Delta\nu = 562 \text{ cm.}^{-1}$ in *o*-kresyl acetate and 560 cm.^{-1} in methyl and ethyl salicylate were observed with the same intensity. And both the frequencies of $\Delta\nu = 571$ and 616 cm.^{-1} were observed in ethyl and iso-propyl cinnamates.



$\Delta\nu = 562 \text{ cm.}^{-1}$



$\Delta\nu = 560 \text{ cm.}^{-1}$



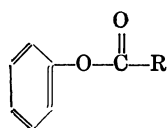
$\Delta\nu = 571, 616 \text{ cm.}^{-1}$

Since all the substances studied contain the C=O group, the comparison of the influences on the frequency due to this linkage seems to be interesting. The lines associated with this linkage are broad, diffuse and intense. The constitutive influences of the substituents attached to the carbonyl group have been studied by Dadiou-Kohlrausch.⁽¹¹⁾ Considering the data we obtained in the previous and the present experiments the following facts are recognized.

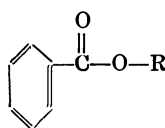
The C:O frequency is directly influenced by an atom or atom group attached directly to it, and independent of the group faraway from it. As shown below, in the cases of phenol esters of fatty acids and *o*-kresyl acetate, the shifts due to the C:O group are practically the same, i.e., 1760 and 1764 cm.^{-1} . So are the cases in the benzoates and the alkyl phthalates, the value of the shift in the latter esters decreases about 40 cm.^{-1} from that of the former.

(10) *Monat. Chem.*, **60** (1932), 253; **61** (1932), 426; Kohlrausch, "Smekal-Raman Effect," 227.

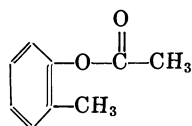
(11) *Ber.*, (B) **66** (1933), 1-12; Kohlrausch, "Smekal-Raman Effect," 157.



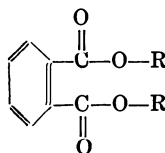
$$\Delta\nu = 1761 \text{ cm.}^{-1}$$



$$\Delta\nu = 1720.$$

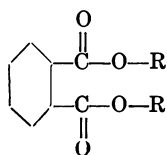


$$\Delta\nu = 1764 \text{ cm.}^{-1}$$

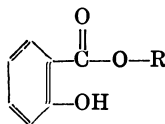


$$\Delta\nu = 1718 \text{ cm.}^{-1}$$

In the case of salicylates, the OH group exerts a remarkable influence on the C:O linkage, even when the OH group is not directly attached to the same carbon atom of the C:O linkage. By the exchange of the $-\text{CO}-\text{O}-\text{R}$ group of alkyl phthalates into OH, the shift decreases from 1718 cm.^{-1} to 1672 cm.^{-1}

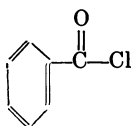


$$\Delta\nu = 1718 \text{ cm.}^{-1}$$

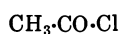


$$\Delta\nu = 1672 \text{ cm.}^{-1}$$

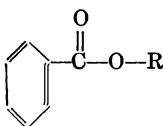
On the other hand, the Cl atom seems to exert an opposite influence on the C:O group. Benzoyl chloride⁽¹⁾ and acetyl chloride⁽¹²⁾ have the high values of 1768 and 1797 cm.^{-1} respectively, compared with the low values of alkyl benzoates and acetyl acetate.



$$\Delta\nu = 1768 \text{ cm.}^{-1}$$



$$\Delta\nu = 1797 \text{ cm.}^{-1}$$



$$\Delta\nu = 1720 \text{ cm.}^{-1}$$



$$\Delta\nu = 1737 \text{ cm.}^{-1}$$

(12) Kohlrausch, "Smekal-Raman Effect," 318.

Thus the difference between the frequencies of C=O linkage in esters and the corresponding acid chlorides is about 50 cm.^{-1}

It was observed that the intensities of the frequencies due to the C=O linkage are strong in the case of esters of benzoic acid, cinnamic acid, phthalic acid, salicylic acid and benzoyl chloride, but weak in the case of phenol esters of fatty acids, alkyl esters of phenylacetic acid and ethyl ester of phenyl propionic acid. The difference of the intensities of these two kinds is so distinct that we can recognize it even under the visual measurement. It may be considered, in this case, that the $\text{C}=\text{C}$ - attached to the $\text{C}=\text{O}$ group strengthens the intensity of the latter linkage.

The frequency of $\Delta\nu=804$ in methyl salicylate and that of 814 cm.^{-1} in dimethyl phthalate seems to be corresponded to that of 814 cm.^{-1} in methyl benzoate⁽¹⁾ which may be attributable to the frequency of the system of $\text{C}=\text{O}-\text{O}-\text{CH}_3$. In ethyl salicylate and diethyl phthalate, the frequencies of 845 and 843 cm.^{-1} have been observed, which may be attributable to the vibration of the system $\text{C}=\text{O}-\text{O}-\text{CH}_2-$ as in the case of ethyl benzoate.⁽¹⁾ A very weak line of $\Delta\nu = 845$ in methyl salicylate observed may be considered as due to its impurity. These two kinds of frequencies were observed also in methyl- and ethyl-phenylacetates. They were, however, broad and

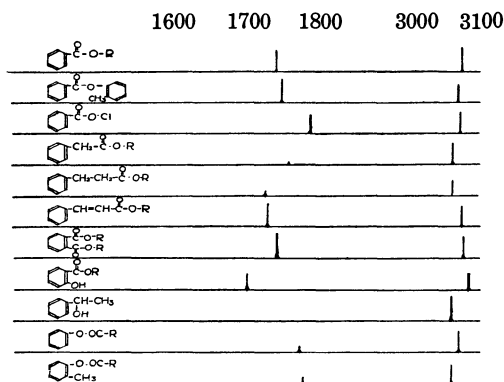


Fig. 1.

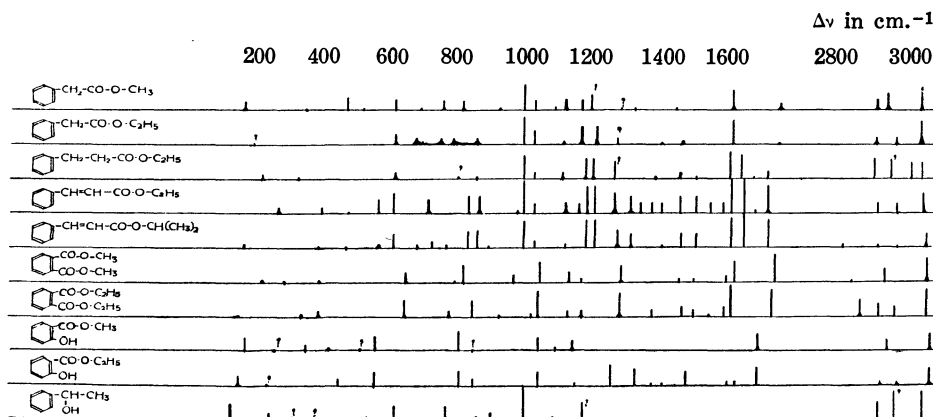


Fig. 2.

diffuse, moreover, on account of the strong back ground appeared on the plates, the measurement could not be done exactly.

Two frequencies of 836, 867 cm^{-1} in ethyl cinnamate and 814, 867 cm^{-1} in iso-propyl cinnamate were clearly observed. It may be explained that the lower frequencies, viz., 836 in ethyl- and 814 cm^{-1} in iso-propyl cinnamates, are arising from the same origin mentioned above, namely that they are caused by the $-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{CH}_2-$ or $-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{CH}_3$ group, but the higher one, viz., 867 in both cases is caused by other linkage of the molecular rest. The confirmation on the facts however, will be made in near future, by studying the corresponding acid and other compounds.

The frequency of 763 cm^{-1} in methyl phenyl carbinol is estimated as the vibration between benzene ring and the carbon atom attached to it. The reason is this. The same frequency is observed in all the substances which have a vibration system, benzene ring and an attaching carbon like ;

$\text{C}_6\text{H}_5-\text{C}-\text{X}$, such as cinnamates, $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{R}$, ethyl phenyl propionate, $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{R}$, alkyl phenyl acetates, $\text{C}_6\text{H}_5-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{R}$, *o*-kresyl benzoate, $\text{C}_6\text{H}_4(\text{CH}_3)-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_5$, *o*-kresylacetate, $\text{C}_6\text{H}_4(\text{CH}_3)-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$, as shown in these experiments. Toluol, ethyl benzol and phenyl nitromethane⁽¹³⁾ etc. have also the same shift in their Raman spectra.

Summary.

(1) The Raman spectra of methyl phenylacetate, ethyl phenylacetate, ethyl phenylpropionate, ethyl cinnamate, iso-propyl cinnamate, dimethyl phthalate, diethyl phthalate, methyl salicylate, ethyl salicylate and methyl phenyl carbinol were studied.

(2) The constitutive influences exerted on the C—H of the benzene ring were observed. It was found that the carbon with the double bond ($-\overset{\text{O}}{\parallel}\text{C}-$) attached to the benzene ring ($\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}\text{C}-$), such as in the case of $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{R}$ and $\text{C}_6\text{H}_5\cdot\text{CH}=\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{R}$ gave the higher frequency ($\Delta\nu = 3070$) than that ($\Delta\nu = 3055$) in the case of $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\overset{\text{O}}{\parallel}\text{C}-\text{O}\cdot\text{R}$ and other

(13) Kohlrausch, "Smekal-Raman Effect," 329-332.

compounds of the type, $C_6H_5 \cdot CH_2 - X$ which have no carbon with double bond directly attached to the benzene ring.

(3) The constitutive influences exerted on the carbonyl group were observed.

(4) Disappearance of 615 cm.^{-1} in derivatives and appearance of 560 cm.^{-1} in salicylates, *o*-kresyl acetate, *o*-kresyl benzoate and cinnamate were observed.

(5) Estimation of the valency frequencies of the $-C(=O)-CH_2-$ linkage was confirmed.

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BEHAVIOUR OF THE SURFACE OF THE SOLUTION OF ELECTROLYTE AGAINST ELECTRONIC IMPACTS.

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Introduction.

The glow-discharge between the surface of the solution of an electrolyte and the metallic cathode, which is suspended above the solution, has been investigated by various authors. The earliest literature is that of Gubkin.⁽¹⁾ He used the solutions of zinc sulphate, silver nitrate and potassium chloroplatinate and obtained respectively zinc oxide, metallic silver as striped dark rings at the surface of the solution under the metallic cathode and the metallic platinum in finely divided form. Günther-Schulze⁽²⁾ studied on various sorts of salt-solutions and obtained oxides and hydroxides in the neutral solutions. According to his view, the electrons accelerated in the electric field between the cathode and the surface of the solution and impinged on the surface do not discharge directly the cations of the solute but the hydrogen ions in the solution, and the residual (OH) react chemically with the cations to form the oxides or the hydroxides. Corbino⁽³⁾ who obtained the metallic powder using copper sulphate, silver nitrate and potassium chloroplatinate as the electrolytes, informed that the chief difference between the process of the ordinary electrolysis and that of the glow-electrolysis lies upon the character of the deposition, the latter being apt to give colloidal solutions of metals.

Haber and Klemenc,⁽⁴⁾ Makowetzky,⁽⁵⁾ and Klemenc and Hohn⁽⁶⁾ investigated the efficiencies of the oxidation and reduction by the electrolysis using the anode or cathode in the gaseous space above the solu-

(1) Gubkin, *Pogg. Ann. Phys.*, **32** (1887), 114.

(2) A. Günther-Schulze, *Z. Electrochem.*, **12** (1903), 833; **30** (1924), 289; **31** (1925), 187.

(3) O. M. Corbino, *Atti acad. Lincei, Roma*, **6**, **5**. (1927), 377; *Chem. Abstr.*, **21** (1927), 2437.

(4) F. Haber u. A. Klemenc, *Z. Electrochem.*, **20** (1914), 458.

(5) A. Makowetzky, *Z. Electrochem.*, **17** (1911), 217.

(6) A. Klemenc u. H. F. Hohn, *Z. Electrochem.*, **37** (1931), 742; *Z. physik. Chem.*, **130** (1927), 378; *Z. physik. Chem.*, **A-154** (1931), 385; **A-166** (1933), 356.

tion and immersing the other electrode in the solution. They found that the efficiencies of the current were larger than that calculated by Faraday's law. Klemenc and Hohn attributed this characteristic behaviour of the glow-electrode to the photochemical action induced by the light emitted by the hydrogen accompanied by the neutralization of the hydrogen ions which were drawn out from the solution into the gaseous space by the potential difference due to the space-charge above the solution. Recently they informed that it is due to the neutral particles e.g. atomic hydrogen, which are produced by the glow-discharge in the gaseous space.

The present authors carried out the glow-electrolysis with the cathode above the solution or the solution covered with a thin film of oil. In the latter case, as the thickness of the oil layer was very thin, it is conceivable as being considerably transparent even against the ultra-violet light, while it could act as an energy absorber against the electrons and the decomposition products of water vapour, if the characteristic properties of the glow-electrode are due to the impacts of them. From the results of such a glow-electrolysis it was concluded that it is not the effect of photons. Hence, it is necessary to decide whether it was caused by the electrons or by the decomposition products of water vapour. In order to distinguish the characteristic behaviour of the surface of the solution against the electronic impacts in comparison with the metallic surface, the authors undertook the differential measurements employing a hot cathode as the source of electrons.

Experimental.

(1) **Glow-Electrolysis.** The apparatus employed for the glow-electrolysis is shown in Fig. 1. The discharge-cell (D) is a U-tube to the one end of which the cathode, an aluminium or a platinum wire, is held by a binding post and to the other the anode is immersed in the solution. A copper coulometer (C) is connected in series to the cathode of the discharge-cell so that the weight increase of the cathode in the coulometer should show the total electricity passed through the cell. The potential difference (E') between the cathode terminal of the coulometer and the anode of the discharge-cell is measured by the vacuum tube voltmeter (V) and is regulated by the resistances (R') and (R'') which are connected in series and in parallel to the supply unit respectively. The potential drop due to the internal resistance of the coulometer can be neglected as it is so small compared to (E') that (E') can be considered as the potential difference between the cathode and the surface of the solution in the discharge-cell.

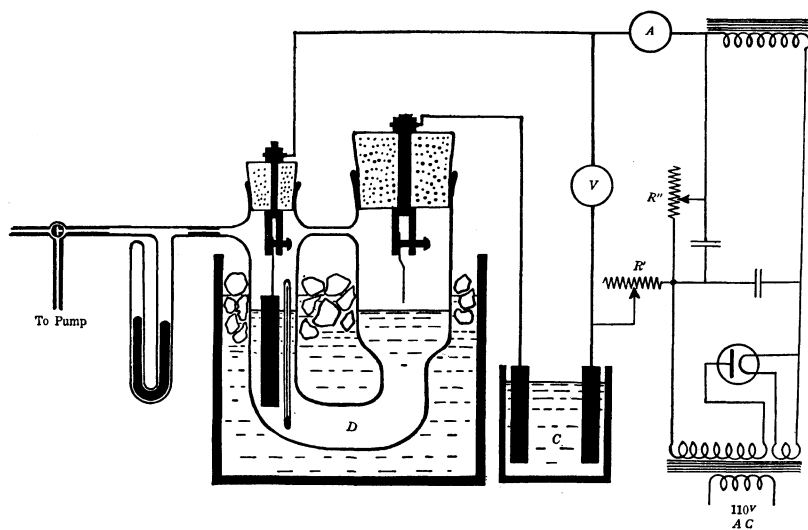


Fig. 1.

Table 1.

Electrolyte	Product	Weight of product mg.	Coulomb. Cu-eq. mg.	Coulomb-Efficiency %	Volt.	Current m.a.
CuSO ₄	Cu(OH) ₂	13.9	11.9	76	550	14.7
		15.8	12.3	84	510	20
	Cu ₂ (OH) ₂	18.7	13.5	90	480	21
		16.0	9.6	108	550	28
		8.5	7.5	74	550	10
ZnSO ₄	ZnO, Zn, Zn(OH) ₂	11.4	12.7	87	540	19
		4.1	7.0	57	500	7.5
		6.7	9.0	72	510	25
		7.4	11.8	61	520	15
		11.0	12.9	84	580	13
		3.0	5.4	54	560	12
		5.6	5.2	104	510	13
		2.5	2.5	104	630	3
ZnCl ₂	ZnO, Zn, Zn(OH) ₂	5.2	5.3	96	560	9
HgCl ₂	HgO & white ppt.	10.7	5.8	—	650	6.5
		4.6	2.4	—	695	2.2
Pb(NO ₃) ₂	PbO	37.5	17.6	61	410	19
MnSO ₄	Mn ₃ O ₄	7.1	5.1	—	570	10
NiSO ₄	Ni(OH) ₂ & black ppt.	15.0	13.9	—	500	25

The electrolytes used for the glow-discharge are shown in the first column of Table 1. As products, hydroxides were obtained, as a rule; however, when the oxides are more stable they were also formed, as shown in the second column of the same table. Most of them appeared in the form of cloud under the cathode in the solutions. In the case of zinc salts, the metallic zinc was observed besides the hydroxide and the oxide which deposited in the form of ribbons of thin films. The mechanism of the formation of the metallic zinc can be considered as the same as that when the surface was covered with liquid paraffin.

In this case, the deposits and the solution in the discharge-cell were taken out and filtered with a paper, the residue was washed down in a beaker, then all the products were dissolved in an excess of diluted sulphuric acid which was previously standardized with a normal solution of caustic soda and the excess of the acid was titrated with the same alkali solution using methyl orange as the indicator.

The chief deposits in the solution of copper sulphate were of two kinds, the greater portion was the greenish blue cupric hydroxide and the smaller was the yellow cuprous hydroxide, their proportion varied largely. The formation of metallic copper was almost imperceptible. In the table the weights were given as cupric hydroxide.

When the surface of the solutions were covered with thin films of liquid paraffin neither hydroxide nor oxide was observed, but the finely divided powders of metals were obtained. When silver nitrate was used as an electrolyte, a brilliant mirror of metallic silver was observed besides the fine powders in the solution. Moreover, the thin layer of liquid paraffin showed an intense bluish green fluorescence during the electrolysis.

(2) Discharge with Hot Cathode. In order to distinguish the characteristic behaviour of the surface of the solution against the electronic impacts from that of the metallic surface, it is necessary to remove the effects of the gaseous space; for this purpose, the authors undertook the differential measurements with the arrangement as shown in Fig. 2.

In the discharge-cell a filament used as the hot cathode was placed in the gaseous space parallel to the surface of the solution which serves as an anode and a nickel plate which serves as an auxiliary anode. The distances from the hot cathode and the two anodes must be equal as far as possible.

The two internal resistances i.e. the resistance between the hot cathode and the surface of the solution, and that between the hot cathode

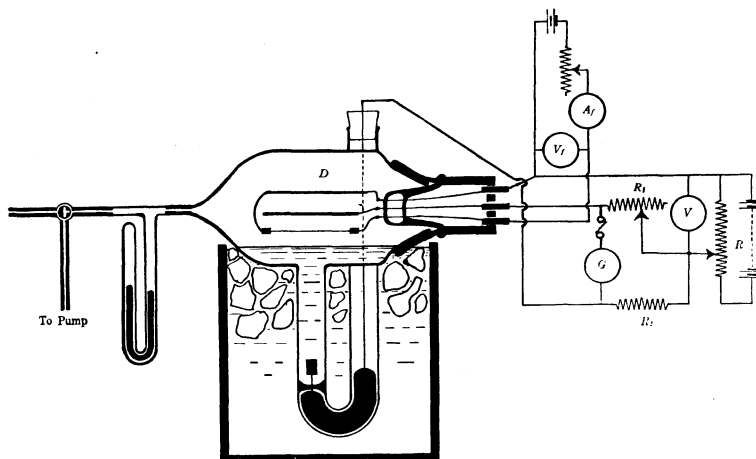


Fig. 2.

and the metallic anode form the arms of the Wheatstone's bridge with two external resistances (R_1) and (R_2) which are much smaller than internal ones. The potential difference applied between the hot cathode and the two anodes, which is regulated by the potentiometer (R), can be regarded as indicated by the voltmeter (V). The value of (R_1) in the equilibrium of the bridge which is determined by the galvanometer (G) gives the current ratio in an arbitrary unit, provided (R_2) is kept constant, throughout these measurements (R_2) was fixed at 5734 ohms.

As the hot cathode, a platinum coated with barium oxide or a blank platinum wire was used, this was heated by the electric current whose intensity and terminal voltage were measured respectively by the ammeter (A_f) and the voltmeter (V_f).

The inside of the discharge-cell should be absolutely free from oils and greases, if there is a slight trace of them, the anode process is very much affected, showing the similar behaviour as when covered with liquid paraffin. The solutions must be brought into reduced pressure before introducing in the discharge-cell to avoid the risk of bubbling in the cell due to the dissolved gas. The hot cathode and the auxiliary anode were then fitted and the gas above the solution was exhausted at ca. 100 mm. of mercury, cooled to the temperature slightly above the freezing point of the solution and exhausted the gas once more to 5–15 mm. of mercury.

On account of too high pressure for such experiments, if the currents were not so small, it was liable to form the space charge. In this experiments, the thermo-electronic currents were about the order of 10^{-6} ampère. Therefore, the imperfection of the compensation of the effect of the space charge due to the inexactitude of the location of the hot cathode was able to lessen.

The current ratio was measured with respect to E , the accelerating potential difference for electrons impinging on the surface of the solution and the nickel plate as described above. As represented in Fig. 3 a-c each of the diagrams showing the relation between the current ratio and E shows a maximum at E'_m . The values in these diagrams, as well as in the table were corrected with a half value of the terminal voltage of the hot cathode. In the case the blank platinum wires used as the hot cathodes, the maxima were given in the vicinity of 17 volts, whereas in the case of the platinum wire coated with barium oxide, the maxima were found in the neighbourhood of 22 volts. This discrepancy is due to the difference in the initial velocities of the electrons emitted from the hot cathodes. The initial velocity of the electrons ejected by the platinum is 6.27 volts,⁽⁷⁾ hence the E'_m obtained on the diagrams using blank platinum wires was corrected with this value. The value of correction applied for the E'_m , using platinum wire coated with barium oxide was 1.69 volt.⁽⁸⁾ These values are tabulated in Table 2, the corrected values of E'_m of both cases denoted by E_m , coincide with each other. With the most kinds of solutions employed in this experiment, every E_m is found about 23 volts, except in the case of ammonium sulphate the value is somewhat higher. When the surface of the solution was covered with a very thin film of liquid paraffin the curve takes a steadily increasing form as shown in Fig. 3-d.

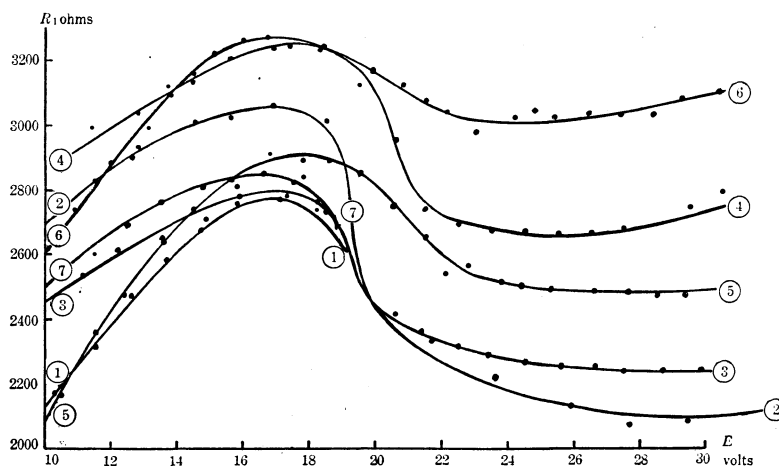


Fig. 3 a.

(7) Du Bridge, "Landolt-Börnstein-Ross-Scheele Tabellen," Eg. II. 5-Aufl.

(8) Michel u. Spanner, "Landolt-Börnstein-Ross-Scheele Tabellen," Eg. I. 5-Aufl.

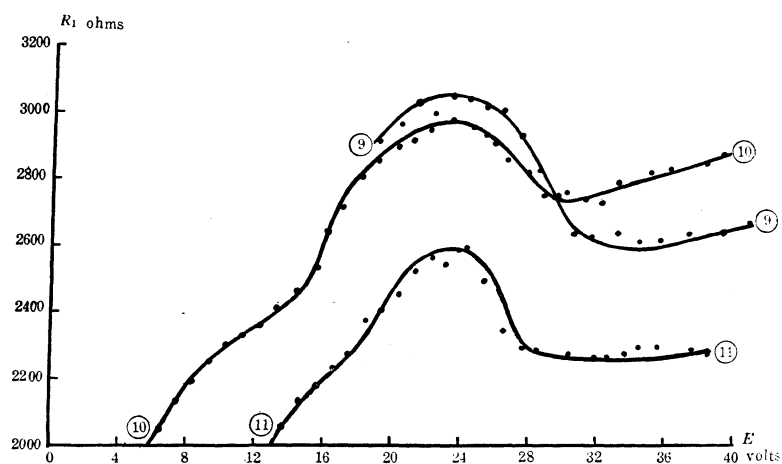


Fig. 3b.

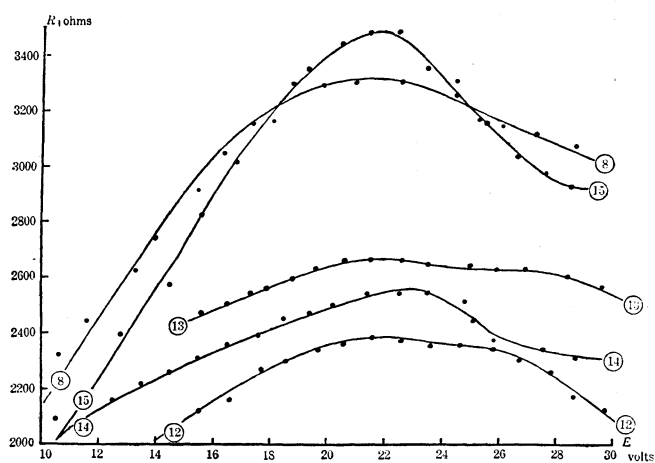


Fig. 3c.

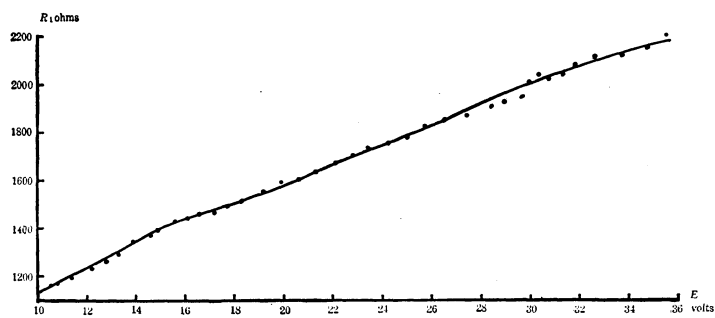


Fig. 3d.

Table 2.

Electrolyte	E'_m	Initial vel. correction	E_m	Curve No.
H_2SO_4	16.6	6.27	22.9	1
	16.8		23.1	2
$(\text{NH}_4)_2\text{SO}_4$	16.9	6.27	23.2	3
	17.5		23.8	4
	17.8		24.1	5
CuSO_4	16.8	6.27	23.1	6
	17.0		23.3	7
H_2SO_4	21.5	1.69	23.2	8
$(\text{NH}_4)_2\text{SO}_4$	23.2	1.69	24.9	9
	23.7		25.4	10
	23.5		25.2	11
K_2SO_4	22.0	1.69	23.7	12
	21.8		23.5	13
NiSO_4	22.9	1.69	24.6	14
	21.8		23.5	15

Discussion of Results.

(1) **Glow-Electrolysis.** The formation of hydroxides and oxides at the surface of the solution as the products of glow-electrolyses suggests the decomposition of the water molecules; however, it is still in question whether the water molecules to be decomposed belong to the gaseous space or to the solutions, and it is also to be determined in what form the energy is required for the decomposition of the water molecules. Experiment shows the coulomb-efficiencies of the formation of hydroxides or oxides are not so small that it can not be considered as by the mere migration of neutral particles from the gaseous space into the solution, except in the case when the particles have enough energy to dissociate the water molecules in the solution. At any rate the decomposition of the water molecules should also occur at the surface of the solution. Since the cupric hydroxide can be reduced by the nascent hydrogen generated by the decomposition of the water molecules in the solution, the formation of the cuprous hydroxide seems to support this consideration.

The form of the energy is now to be discussed. It may be (1) as photons of ultraviolet region, or (2) the energy possessed by the elec-

trons or (3) by the decomposition products of water vapour. From the facts that the products by the glow-electrolyses of the solutions covered with thin films of oil are entirely different, it must be regarded as it is not by the photons, because the thin films are not entirely impenetrable to the ultraviolet light. If it is the second case, the electrons should acquire enough energy for the dissolution of the water molecules at the surface of the solution before they collide with the surface. However, when the surface is covered with a thin film of oil the kinetic energy of electrons should be absorbed by the oil molecules, and the debilitated electrons set on the film attracting the cations in the solution to form an electric double layer, the strength of which increases until it discharges to deposit the cations in the metallic form similar to the ordinary electrode process.

It may be also explained by introducing the particles produced by the decomposition of water vapour. However, in order to play this rôle, the particles should have rather a long period of average life in their highly excited state which lies sufficiently high above their normal level for the multiple decomposition of water molecules without further acceleration against the particles produced by the decomposition. If it were the case, it may be interpreted as follows. By the collisions of excited particles the dissociation of water molecules take place, which results the deposition of the cations as hydroxides or oxides; however, when the surface of the solution is covered with a thin film of oil, the particles are isolated from the solution, hence the characteristic behaviour of the glow-electrode disappears.

As mentioned above, the most probable of the three cases is the second, and the third is also possible.

(2) **Discharge with Hot Cathode.** The ionization and dissociation in the gaseous space above the solution by the glow-electrolysis are obvious,⁽⁹⁾ where the dissociation of the water molecules situated at the surface of the solution is necessary, the latter is presumed to have direct contribution to the characteristic behaviour of the glow-electrode. The cause of this dissociation at the surface is now to be discussed. If it were caused by the electrons, there should be an abrupt increase of the electric conductance at the boundary of the gas and the solution by the dissociation of the water molecules, which gives rise to the deposition of the cations when the kinetic energy of electrons attain a certain value

(9) W. R. Cousins, *Z. physik. Chem.*, B-4 (1929), 440; G. I. Lavin & F. B. Stewart, *Nature*, 123 (1929), 607; K. F. Bonhoeffer & T. G. Pearson, *Z. physik. Chem.*, B-14 (1931), 1. They found OH-band in the emission of gas by the glow-discharge.

E_m . The number of electrons accepted by the metallic anode increases proportionally to the three halves power of E , while the number of the electrons accepted by the surface of the solution is small compared to the former until the potential difference E is raised to E'_m , and in the vicinity of E the number suddenly increases to some extent, but after E exceeded E'_m the number does not increase so abruptly as before.

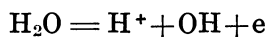
However, if it were caused by the excited particles produced in the gaseous space by the collisions of the electrons with water molecules, the probability of the formation of such particles should increase as E is raised, because the formation is possible in the zone between the position, where the electrons will gain enough energy to dissociate and excite the water molecules and the surface of the solution. Hence the current should increase gradually as E is raised.

The current in the discharge-cell involves three factors with respect to the potential difference E , the first of them is the effect of the external field on the emission of the hot cathode, the second is the effect of the gaseous medium e.g. formation of space charge etc., and the third is the effect caused by the transportation of negative electricity through the boundary of the gas and the solution. By means of the differential measurements, informed above, the first and the second effects can be removed and the third effect is only admitted in its relative appearance against the metallic surface.

Therefore, if the abrupt increase of the electric conductance at the boundary were caused by the electrons, there must be a maximum on the curve representing the relations between the current ratio and the potential difference E at E'_m ; however, if it were by the excited particles, there should not be any maximum on the curve. This maximum was verified with each of the solutions of the electrolytes used in the experiment, as described above. The existence of the maxima offers a proof that the decomposition of the water molecules situated at the surfaces of the solutions should be caused by the impacts of electrons and not by the secondarily produced particles produced by the collisions of the electrons emitted by the hot cathode with the water vapour. As the mean, the value $E = 23.8$ volts was given within the error of 1.6 volt by this experiment, and this value can be interpreted in the following manner.

Ascribing the abrupt increase of the electric conductance of the boundary determined by the maxima on the curves representing the relation between the current ratio and the potential difference applied between the hot cathode and the both anodes to the dissociation of the

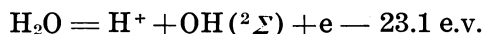
water molecules situated at the surface of the solution, the dissociation is assumed as:



where the OH molecule may be excited to $^2\Sigma$ state. The energy required for this dissociation can be obtained as follows.

- (1) $\text{H}_2\text{O}(\text{l}) = \text{H}_2\text{O}(\text{g}) - 0.47 \text{ e.v.}$ Heat of vapourization of water/molecule at 0°C .⁽¹⁰⁾
- (2) $\text{H}_2\text{O}(\text{g}) = \text{H} + \text{OH}(^2\Pi) - 5.1 \text{ e.v.}$.. Heat of dissociation of water/molecule⁽¹¹⁾
- (3) $\text{OH}(^2\Pi) = \text{OH}(^2\Sigma) - 4.03 \text{ e.v.}$ Energy of excitation of OH/molecule⁽¹²⁾
- (4) $\text{H} = \text{H}^+ + e - 13.53 \text{ e.v.}$ Ionization potential of hydrogen atom.

Accordingly, the sum of these equations (1), (2), (3) and (4) gives



The experimental result showed a good agreement with this value.

The excited OH molecules at $^2\Sigma$ state will immediately drop to the normal level and combine with the electrons by their strong affinities; then the negative electricities are transformed into the ionic forms which are readily soluble in the solution and the OH^- ions react chemically with the cations to form the hydroxides or oxides of metals.

Summary.

(1) The glow-discharge between the metallic cathode and the surface of the solution was examined, and it was found that the products were mostly hydroxides or oxides of the cations in the solution. From the coulomb-efficiencies of their formations and the products obtained by the glow-electrolyses with the solutions covered with oil, it was concluded that the decomposition of water molecules should occur at the surface of the solution and it should be caused by the impacts of the electrons

(10) W. Schüle, "Landolt-Börnstein-Ross-Scheele Tabellen," Eg.I. 5-Au. 594.8 cal/gr. is given.

(11) Senftleben u. Reichmeier, *Phys. Z.*, **34** (1933), 228.

(12) Calculated from the water-band at 3064 A.U. M. Kimura, *Sci. Pap. Inst. Phys. Chem. Res. Japan*, **18** (1932), 109 offered 71410 cm^{-1} for the dissociation $\text{H}_2\text{O} \rightarrow \text{OH}(^2\Sigma) + \text{H}$.

or other particles having enough energies to dissociate the water molecules.

(2) A characteristic phenomenon by the transportation of the negative electricity through the boundary of the gas and the solution was studied and it was deduced that the dissociation should be caused by the accelerated electrons having the kinetic energy of 23.8 e.v. .

Further, the process of the dissociation was proposed, and the energy required for this dissociation was calculated as 23.1 e.v. .

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ON THE COPPER AGE IN ANCIENT CHINA. III.

By Tsurumatsu DÔNO.

Received January 13th, 1934. Published March 28th, 1934.

In the previous two reports,⁽¹⁾ the present author described the results of chemical analyses of several ancient Chinese weapons which consist of almost pure copper and concluded that the copper age and a transitional period to the well known bronze age really existed in ancient China. Quite recently the author was fortunately able to get in hand some further specimens of old Chinese weapons of the same type as already studied, by the kindfull efforts of Mr. Mikami and Mr. Sugimura in Peiping, to whom the author wishes to express his profound indebtedness on this occasion.

The newly obtained specimens consist of a spear head and three halberds (compare Figs. 1, 2, 3 and 4.), among which the spear head contains, according to the present investigation, about 0.24% of tin (too insignificant amount in tin to be taken as a bronze implement), while two halberds involve no or a very slight amount of tin, in the latter case the metal being only detectable by the spectral analysis.

As for the last one of these halberds, it showed indeed so much content of tin as 13.74% and it may properly be called a bronze implement. More-

(1) T. Dôno, this Bulletin, **7** (1932), 347; **8** (1933), 133.

over, it is of no less interest to recognise the fact that this last specimen of the high tin content is considered to possess a quite advanced form compared to the others now studied from the archæological standpoint.

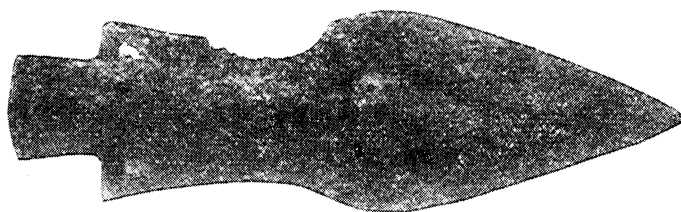


Fig. 1. Spear-head.

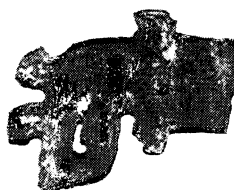


Fig. 2. Halberd A.

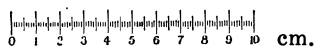
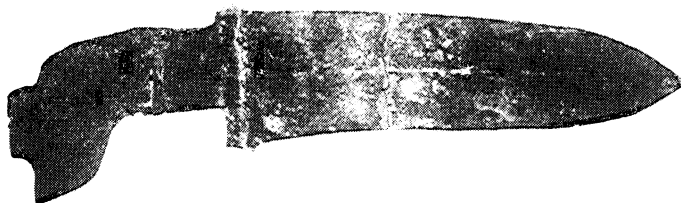


Fig. 3. Halberd B.



Fig. 4. Halberd C.

Experimental Part.

The chemical analyses and the metallographical studies were carried out in the usual way⁽²⁾ and the constituents, which are scarcely detected by the chemical methods, were found from the arc spectral analysis. The results are given below :—

Results of the chemical analysis :

	Spear-head	Halberd A	Halberd B	Halberd C
Sample (gr.)	0.4960	0.5050	0.5007	0.5120
Copper (%)	84.78	88.14	85.86	84.92
Tin (%)	0.24	Trace	Trace	13.74
Lead (%)	6.02	6.64	13.05	0.30
Arsenic (%)	Trace	—	—	Trace
Iron (%)	3.65	0.08	0.06	0.12
Nickel (%)	—	—	—	—
Gold (%)	Trace	Trace	Trace	Trace
Silver (%)	0.06	0.04	0.05	0.04
Total (%)	94.75	94.90	99.02	99.12

Metallographical photographs

(2) T. Dôno, *J. Chem. Soc. Japan*, **51** (1930), 463 ; **53** (1932), 100.

(Enlarged 100 times and etched by the solution of ammoniacal hydrogen-peroxide).

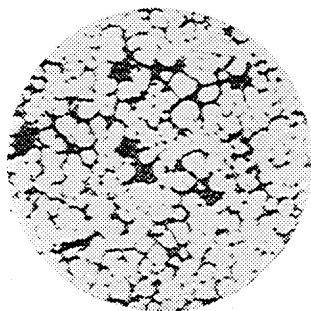


Fig. 5. Spear-head

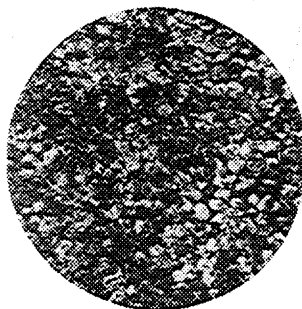


Fig. 6. Spear-head (etched)

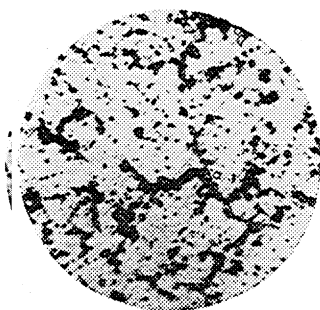


Fig. 7. Halberd A

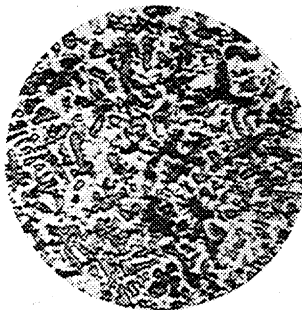


Fig. 8. Halberd A (etched)

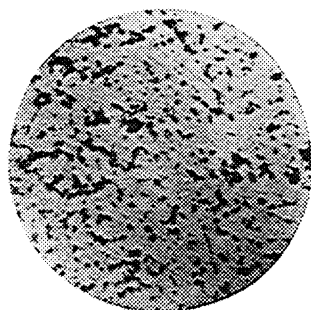


Fig. 9. Halberd B

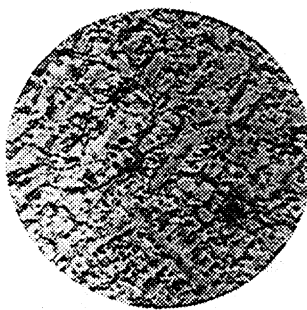


Fig. 10. Halberd B (etched)

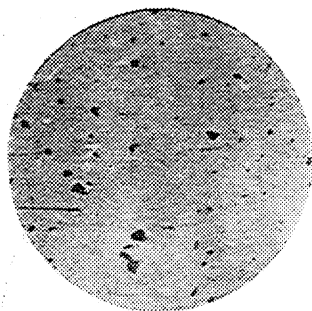


Fig. 11. Halberd C

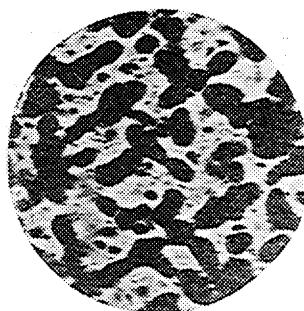


Fig. 12. Halberd C (etched)

As will be seen in the analytical results given above, some of them are considerably less than 100% in total: this is, as was stated in the previous reports,⁽¹⁾ due to oxygen which combined probably with metals during or after the manufacture of these weapons. As for the meaning of the existence of other metals also was already explained in the preceding papers.⁽¹⁾

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. Y. Komai and Dr. N. Egami in the Archaeological Institute of the Faculty of Literature of Tokyo Imperial University, who gave valuable advices on the archæological consideration.

Summary.

One spear-head and three halberds which are of the same types as those relics unearthed from Yin Site, were analysed, and it was proved that the spear-head and the two of three halberds must be called the copper implements, and the last one of the halberds contains a considerable amount of tin, therefore this specimen may be called properly a bronze one.

Considered from these results coupled with those described in the previous two papers, all of four spear-heads already studied were of almost pure copper, and four of the six halberds were also pure copper implements and some others were regarded as bronze implements.

Thus, by the present investigation of the author, the existences of the copper age and a transitional period to the bronze age in ancient China were further emphasized.

Chemical Laboratory, Akita Mining College.

THE MEASUREMENT OF HIGH VOLTAGE OF ALTERNATING CURRENT BY KERR CELL.

By Yohei YAMAGUCHI and Kunimoto MIYAMOTO.

Received December 23rd, 1933. Published March 28th, 1934.

Introduction.

Many experiments have been carried out on the double refraction of nitrobenzene in the electric field by several authors, and its Kerr constant was evaluated by different methods. The present authors tried to evaluate the voltage applied to the electric field by using the known Kerr constant and the intensity of light which was passed through the Kerr cell of nitrobenzene placed in crossed nicols and simultaneously in the field of 7,000–25,000 volt/cm. and of 50-cycle of alternating current.

Experimental.

Apparatus. The glass vessel which holds nitrobenzene has a capacity of 8 cm. $\times$ 2 cm. $\times$ 3.5 cm. In order to pass the light through the vessel a hole of 6 mm. of diameter is made on each wall of 2 cm. $\times$ 3.5 cm. and it is covered with a sheet of deck glass which is fixed at the wall with bakerite varnish by gently heating after dried. Two copper plates of 0.3 mm. of thickness and 71.0 mm. $\times$ 6.0 mm. of area are put parallel with each other with 0.38 cm. of width and these two are fixed perpendicularly on the thick glass cover of the vessel and are used as electrodes. It is necessary to use some sealing materials to make the cover tight with the vessel in order to prevent the absorption of moisture into nitrobenzene. Such materials as vaseline, however, are not appropriate, as they are soluble in nitrobenzene. Therefore the above glass vessel is put into a larger glass vessel (9 cm. $\times$ 3.5 cm. $\times$ 6.0 cm.) having as well windows to admit light as before. Phosphorus pentoxide is put on the bottom of the outer vessel to absorb moisture in the vessels.

A gas-filled tungsten filament lamp of 100-volt and 100-watt is illuminated by secondary batteries as the light source. The light is condensed by a lens and is made approximately a monochromatic light by the filter of 510–540 $\mu\mu$. The light passed through the slits and a polarizer of nicol is admitted into nitrobenzene in the glass vessel. The double refracted light in nitrobenzene is passed through an analyser and is fallen on a dry plate in a special camera, and a spot of 2.0 mm. of

diameter is made on the plate. The dry plate is shifted a little after each experiment to obtain a series of spots on the plate. The dry plates used were Ilford screened chromatic H.D. 270.

The time of exposure of the dry plate was 5–10 sec. The accuracy to 0.05 sec. of time of exposure was obtained by using the time of flow of a certain quantity of an aqueous solution of glycerine through a capillary tube. The angle of rotation of the analyser was read with a magnifying lens.

Electric high potentials were obtained from the transformer with the turn ratios of 30, 50, 75 and 100. Alternating current of 110-volt and 50-cycle was supplied to the primary circuit of the transformer and it was controlled to 100 volts.

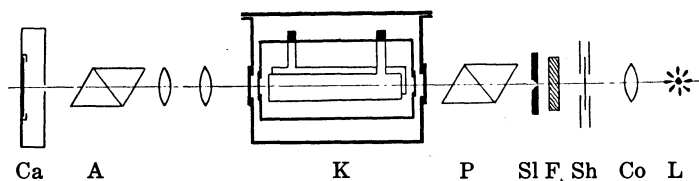


Fig. 1.

The apparatus used is illustrated in Fig. 1. L is the light source, Co condenser, Sh shutter, F filter, Sl slit, P polarizer, K Kerr cell, A analyser and Ca camera.

Nitrobenzene used was the pure chemicals of Kahlbaum, and it was purified as follows. Nitrobenzene (500 gr.) was distilled at 130°C. under a reduced pressure by passing dry air from the capillary. The distillate was frozen by freezing mixture and the part which did not melt at 1.0°C. was collected. This part was put into a distilling apparatus whole of which consisted of glass, and it was distilled without boiling under 2 mm. pressure by heating one part of the vessel below 90°C. and by cooling the other part with freezing mixture. About 100 c.c. of thus purified nitrobenzene was obtained and kept free from atmosphere in the dark.

Experimental Procedure. Nitrobenzene is sealed in the cleaned vessel. The position of the polarizer is so adjusted as its plane of polarization makes the angle of 45° to the plane of electrode. The camera is unmounted and the analyser is rotated until the visual field is just dark to the naked eye. The camera in which the halved dry plate is placed is mounted on the apparatus and a high potential is applied on the electrodes. A requisite time of exposure is given to the dry plate by opening the shutter. The dry plate is shifted a little and another exposure

is carried out as before by changing the potential. A series of points of exposures is thus obtained on a sheet of dry plate.

The darkness of the spots of the dry plate is not proportional to the intensity of light fallen on it. Therefore the spots of standards for the comparison of darkness with intensity of light were made on the dry plate of the other half by changing the angles of polarization between the polarizer and the analyser to 90° , 80° , 70° , 60° , 50° , 40° , 30° , 20° and 10° with the equal time of exposure and with no potential on the electrodes of the Kerr cell. The one half of the dry plate used for determining the potentials and the other half of the plate used for obtaining the standards of darkness were developed and fixed together under the same condition. The darkness of the plates was measured with a microphotometer. And the intensity of light fallen on the former plate was determined by comparing with the standard prepared on the latter.

Every one series of experiment was carried out by changing the turn ratios of transformer to 30, 50, 75 and 100, and the standard of darkness was prepared in every one series. The voltage of the primary circuit was controlled to 100 volts during the experiments, but the pointer of voltmeter fluctuated between 98 and 102 volts. Although the temperature varied 10 – 15°C . in the experiments, its effect, however, was not taken into the calculation.

Intensity of Light. When a potential is not applied to the Kerr cell, if α denote the angle of polarization between the polarizer and analyser, and I_α denote the intensity of light from the analyser, and $I = 1$ when $\alpha = 0^\circ$, then there is the following relation.

$$I_\alpha = \cos^2 \alpha .$$

The darkness of the standard dry plate is read with the microphotometer and a curve relating between the reading and I_α is drawn. The intensity of light fallen on the dry plate used for the determination of potential is determined with the reading of the microphotometer by using the above curve. If the product of mean intensity of light and time of exposure, i.e. light quantity is equal each other, it is assumed that the darkness of the dry plate is the same, though the mode of change of intensity of light may be different in the course of exposure.

Relation between Voltage and Intensity of Light. Since an alternating current of 50-cycle is used and the time of exposure of the dry plate is 5–10 sec., the intensity of light varies periodically in the course of exposing and the mean of intensity is recorded on the dry plate. Hence

the effective voltage of A.C. is calculated from the measured mean intensity of light.

When the Kerr cell is put in the crossed nicols and the angle between the plane of polarization and that of electrode is 45° , then the relation between the intensity of light I from analyser and voltage E is as follows.

$$I = \sin^2 \frac{\pi B l E^2}{a^2}$$

where E is the voltage expressed in e.s.u., B the Kerr constant, a the distance between electrodes and l the width of electric field.

If E_t denote the voltage at the time t since the voltage E of A.C. changes with time, I_t the intensity of light at that time, and also ϵ_t the effective voltage when the voltage of A.C. changes in the form of a sine curve, then

$$I_t = \sin^2 \left(\frac{2\pi B l \epsilon^2}{a^2} \sin^2 \omega t \right)$$

If I denote the mean intensity of light with $1/4$ cycle,

$$\begin{aligned} I &= \frac{2\omega}{\pi} \sum_{t=0}^{t=\frac{\pi}{2\omega}} I_t \\ &= \frac{2\omega}{\pi} \int_0^{\frac{\pi}{2\omega}} \sin^2 \left(\frac{2\pi B l \epsilon^2}{a^2} \sin^2 \omega t \right) dt. \end{aligned}$$

When $2\pi B l \epsilon^2 / a^2$ is represented by b ,

$$\begin{aligned} I &= \frac{2\omega}{\pi} \int_0^{\frac{\pi}{2\omega}} \sin^2 (b \sin^2 \omega t) dt \\ I &= \frac{1}{\pi} \int_0^{\frac{\pi}{2}} \{1 - \cos (2b \sin^2 x)\} dx \\ &= \frac{1}{2} - \frac{1}{\pi} \int_0^{\frac{\pi}{2}} [\cos b \cos (b \cos 2x) - \sin b \sin (b \cos 2x)] dx \\ &= \frac{1}{2} - \frac{2}{\pi} \cos b \int_0^{\frac{\pi}{4}} \cos (b \cos x) dx \\ &= \frac{1}{2} \left\{ 1 - \cos \left(\frac{2\pi B l \epsilon^2}{a^2} \right) J_0 \left(\frac{2\pi B l \epsilon^2}{a^2} \right) \right\} \end{aligned}$$

where J_0 indicates Bessel's function.

The value of B at $520\text{ }\mu\mu$ of λ is obtained by the following equation as 374.4×10^{-7} from the value of B ($= 346.0 \times 10^{-7}$) at $546\text{ }\mu\mu$ of λ which was obtained by R. Möller.⁽¹⁾

$$B_{\lambda_1} = B_{\lambda_2} \frac{\lambda_2 n_{\lambda_2} (n_{\lambda_1} - 1)^2}{\lambda_1 n_{\lambda_1} (n_{\lambda_2} - 1)^2}$$

where n is the index of refraction.

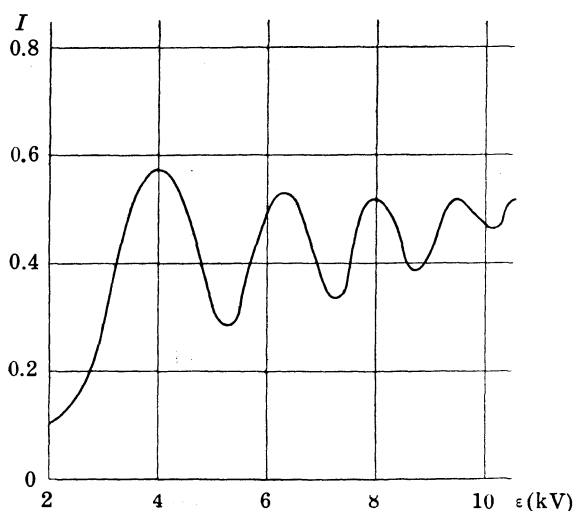


Fig. 2.

The constants of the apparatus are as follows: $a = 0.38$ cm., the length of electrode is 7.10 cm., hence $l = 7.18$ cm. (by calculation). Putting these values in the above equation,

$$I = \frac{1}{2} \{ 1 - \cos(7.45^\circ \epsilon^2) J_0(0.1300 \epsilon^2) \}$$

where ϵ is expressed in kilovolt. The relation between ϵ and I in the range from $\epsilon = 2$ to 10.5 is shown by a curve in Fig. 2.

The Results of Experiment. The effective voltages ϵ'_2 corresponding to the secondary voltages ϵ_2 obtained from the turn ratios of the transformer were calculated from the measured intensity of light by using the curve of Fig. 2. These values are shown in Table 1. ϵ_1 in the table is the effective voltage of the primary circuit, I intensity of light, ϵ_2 effective voltage of the secondary obtained by the turn ratio and ϵ'_2 that obtained from the intensity of light.

(1) *Phys. Z.*, **30** (1929), 22.

Table 1.

ϵ_1	I	ϵ_2	ϵ'_2	ϵ_2/ϵ_1	ϵ'_2/ϵ_1
100.0	0.22	3.000	2.780	30	27.8
„	0.27	„	2.920	„	29.2
„	0.24	„	2.850	„	28.5
„	0.22	„	2.780	„	27.8
„	0.255	„	2.900	„	29.0
80.5	0.21	2.415	2.760	„	33.0
90.0	0.32	2.700	3.050	„	33.9
100.0	0.45	5.000	4.620	50	46.2
„	0.395	„	4.760	„	47.6
„	0.395	„	4.760	„	47.6
70.0	0.33	3.500	3.070	„	49.5
100.0	0.41	7.500	7.510	75	75.1
„	0.43	„	7.550	„	75.5
„	0.40	„	7.500	„	75.0
„	0.40	„	7.500	„	75.0
„	0.34	„	7.300	„	73.0
„	0.42	„	7.520	„	75.2
100	0.43	10.0 0	9.620	100	90.2
„	0.40	„	8.900	„	89.0
„	0.48	„	9.180	„	91.8
71.0	0.52	7.100	6.450	„	90.9
76.0	0.435	7.600	6.780	„	89.3

Discussion of Results. The voltages obtained from the measured intensity of light are nearly equal to the voltage calculated from the turn ratios of transformer, but the former is generally less than the latter. Every value of voltages obtained from the measured intensity of light has a fluctuation of about 3% from their mean. The following few facts may be the main causes of the above fluctuation.

(1) The primary voltage always varied in the range from 1 to 4% in the measurements. (2) The accuracy of the microphotometer used is 3–5%. (3) Light passed through the filter is 510–540 $\mu\mu$, while it is assumed simply 520 $\mu\mu$. (4) There is the error of less than 1% in the value of Kerr constant. According to Hehlgers⁽²⁾ its value considerably

(2) *Phys. Z.*, **30** (1929), 942.

varies with the purity of nitrobenzene. (5) Potential gradient of electric field is not linear in impure nitrobenzene.

Summary.

(1) The monochromatic light of about ($\lambda =$) $520\text{ }\mu\mu$ was passed through nitrobenzene which was put in crossed nicols and in an alternating electric field of 7,000–25,000 volts/cm., and the intensity of light from the analyser was measured.

(2) The potential of the electric field was calculated from the measured intensity of light by using the known Kerr constant.

(3) The calculated values of potentials are nearly equal to those obtained from the turn ratios of the transformer, but are generally less than the latter.

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PICRATES OF CHALCONES AS ORGANIC
MOLECULAR COMPOUNDS.⁽¹⁾

By Tei-ichi ASAHINA.

Received January 15th, 1934. Published March 28th, 1934.

It is well known that unsaturated ketones as chalcones form various molecular compounds,⁽²⁾ among which some picrates were reported by D. Vorländer.⁽³⁾ He classified them as salt-like compounds between α , β -unsaturated ketones and acids, and the following picrates were enumerated by him ;

(1) Read before the ordinary meeting of the Chemical Society of Japan, June 14th, 1930.

(2) P. Pfeiffer, "Organische Molekülverbindungen," (1927) 66-85.

(3) *Ann.*, **341** (1905), 32.

Benzalacetophenone picrate	1 : 2 ⁽⁴⁾
Anisalacetophenone picrate	1 : 2
Piperonilideneacetophenone picrate	1 : 2
Cinnamilideneacetophenone picrate	1 : 2
Anisalpinacoline picrate	1 : 2
Dipiperonilideneacetone picrate	1 : 1

These picrates are formed in combining each molecule of chalcone with two molecules of picric acid, but it is not quite certain whether chalcones other than those mentioned above also combine with picric acid always in this proportion of 1:2. Further it is somewhat uncertain whether these picrates are formed just in the same way as chalcones combine with inorganic acids, as was mentioned by Vorländer.

The cause of formation of a molecular compounds, as a component of which nitrophenols are concerning, may perhaps be considered in various ways ; i.e., we may attribute the point of the molecular linkage of a nitrophenol either to its phenol group, nitro group or to NOOH-radical, which is considered usually in a nitrophenol molecule.

The present study was then undertaken, in order to elucidate these questions.

The method of investigation employed by the author is similar to that proposed by H. Rheinboldt,⁽⁵⁾ only slight modification being done in the shape of the stirring rod. Rheinboldt used a slender glass rod for this purpose, but it occurs creeping-up of the molten material along the wall of observing capillary and some errors are often caused, while the pin-head shaped stirrer devised by the author may avoid this difficulty (compare A and B in Fig. 1).

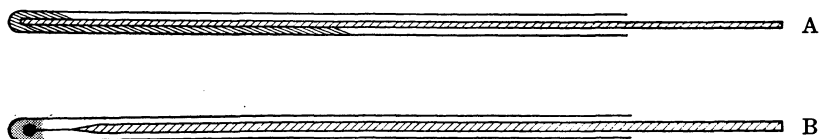


Fig. 1.

The molecular compounds of the chalcones studied by the author were in the following molecular proportions, namely they are not exclusively 1:2;

(4) The figures show the molecular proportions.

(5) *J. prakt. Chem.*, [2] **111** (1925), 242; **112** (1926), 187; **113** (1926), 199.

Piperonilideneacetophenone picrate	1 : 2
2'-Oxybenzalacetophenone picrate	2 : 3
4'-Oxybenzalacetophenone picrate	1 : 1
4'-Ethoxybenzalacetophenone picrate	1 : 1

As β -naphthol gave no molecular compound with piperonilideneacetophenone, it seems that phenols have no affinity with chalcones to form molecular compounds.

Experimental.

3.4-Methylenedioxybenzalacetophenone⁽⁶⁾ was prepared by the condensation of piperonal and acetophenone: 10 gr. of piperonal and 8 gr. of acetophenone were dissolved in 200 c.c. of spirit, and to this solution was added some 5% caustic soda. The separated crystals of feebly yellow colour were recrystallized twice from alcohol: m.p. 121.0°C.

2'-Oxybenzalacetophenone⁽⁷⁾ was prepared by dissolving 2 gr. of *o*-oxyacetophenone and 2 gr. of benzaldehyde in 20 gr. of alcohol and by adding 4 gr. of 50% caustic potash. Evolving a little heat, the solution turned to yellow and then became orange-red and at the same time muddy. After standing overnight it was poured into dilute hydrochloric acid, and then separated chalcone was recrystallized from alcohol: m.p. 88.0–89.0°C.

4'-Oxybenzalacetophenone⁽⁸⁾ was prepared by dissolving one part of *p*-oxyacetophenone and one part of benzaldehyde in 10 parts of alcohol and by adding 2 parts of 50% caustic potash, warming the mixture for half an hour on the water-bath, then pouring it into water and acidifying. The separated chalcone was recrystallized from spirit: m.p. 174.5–175.5°C.

4'-Ethoxybenzalacetophenone⁽⁸⁾ was prepared by ethylation of 4'-oxybenzalacetophenone in the ordinary way with ethyl iodide and caustic alkali: m.p. 73.5–74.5°C.

The *o*- and *p*-oxyacetophenone used in the preceding preparations, were obtained by heating for five hours at 120°C. the mixture of one part of phenol acetate and two parts of anhydrous aluminium chloride, treating the mixture with cold water and then separating the two acetophenones by steam distillation.⁽⁹⁾ The picric acid and the naphthol were purified from the commercial products by repeated recrystallization from water.

(6) St. v. Kostanecki u. M. Schneider, *Ber.*, **29** (1896), 1892.

(7) W. Feuerstein u. St. v. Kostanecki, *Ber.*, **31** (1898), 715.

(8) Kostanecki u. J. Tambor, *Ber.*, **32** (1899), 1924.

(9) K. Freudenberg u. L. Orthner, *Ber.*, **55** (1922), 148.

The system : 3,4-Methylenedioxybenzal-
acetophenone—picric acid (See Fig. 2)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
2.5	97.5	113.5	120.0
4.4	95.6	113.5	116.5
9.2	90.8	113.5	119.8
13.1	86.9	113.5	123.0
19.8	80.2	113.5	126.5
23.0	77.0	113.5	127.2
23.2	76.8	113.0	127.3
32.0	68.0	114.5	128.5
38.3	61.7	104.5	128.0
50.2	49.8	105.0	125.3
61.8	38.2	104.0	117.5
68.0	32.0	104.0	111.0
78.4	21.6	104.3	110.0
83.8	16.2	103.5	113.5
89.8	10.9	104.0	116.5
94.5	5.5	104.5	119.0
100.0	0.0	—	121.0

Eutectic points :

{ 113.5°C. picric acid
 94.5 mol %
 { 104.0°C. picric acid
 27.0 mol %

Distectic point :

128.5°C. { picric acid
 2 mols
 chalcone
 1 mol

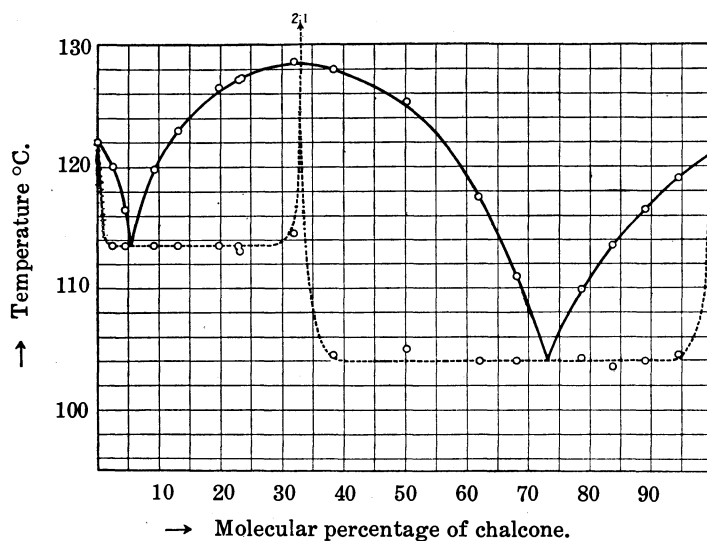


Fig. 2.

The system : 2'-Oxybenzalacetophenone—
picric acid (See Fig. 3)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
5.1	94.9	113.0	118.0
10.2	89.8	113.0	120.5
20.4	79.6	113.0	128.4
24.5	75.5	113.0	129.3
30.5	69.5	113.0	129.5
35.5	64.5	112.0	130.0
38.0	62.0	120.0	130.5
40.6	59.4	110.0	131.0
45.5	54.5	82.5	129.0
50.6	49.4	82.0	127.5
55.6	44.4	82.0	125.8
60.0	40.0	82.0	—
65.4	34.6	82.0	120.0
71.0	29.0	82.0	115.0
80.4	19.7	82.0	103.5
89.8	10.2	82.3	85.0
94.2	5.8	82.5	85.8
100.0	0.0	88.0	89.0

Eutectic points :

{ 113.0°C. picric acid
 92.5 mol %
 { 82.0°C. picric acid
 9.5 mol %

Distectic point :

132°C. { picric acid
 3 mols
 chalcone 2 mols

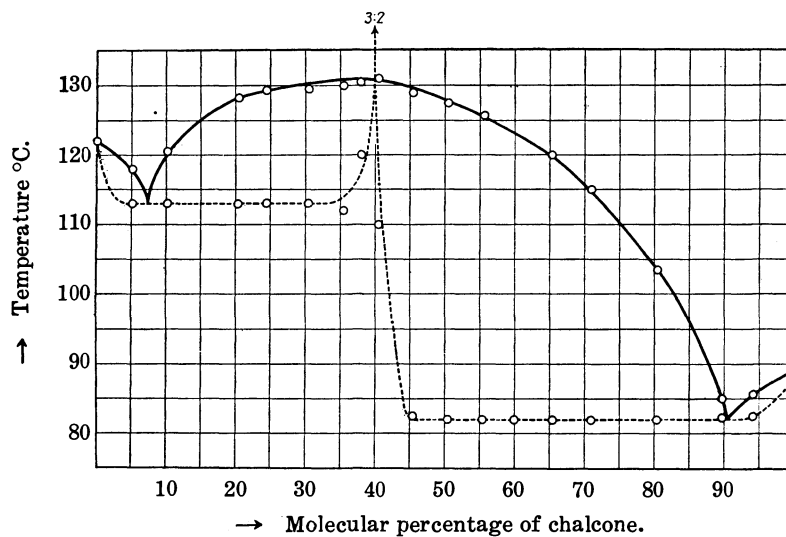


Fig. 3.

The system : 4'-Oxybenzalacetophenone—
picric acid (See Fig. 4)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
2.5	97.5	119.0	119.5
6.5	93.5	119.0	134.3
10.2	89.8	118.0	139.5
16.6	83.4	119.0	145.3
21.0	79.0	119.0	148.0
25.4	74.6	119.5	151.3
30.5	69.5	118.5	153.0
33.0	67.0	120.0	154.0
35.5	64.5	125.0	155.0
40.5	59.5	135.0	156.8
45.5	54.5	141.0	157.0
50.0	50.0	150.0	157.5
55.3	44.7	149.0	156.4
60.5	39.5	150.0	156.2
64.3	35.7	148.0	155.0
68.0	32.0	150.0	158.0
70.1	29.9	149.0	159.5
74.5	25.5	149.0	164.5
88.1	11.9	148.0	170.8
100.0	0.0	174.5	175.5

Eutectic points :

{ 119.0°C. picric acid
 97.5 mol %
 { 149.5°C. picric acid
 37.5 mol %

Distectic point :

157.5°C. { picric acid
 1 mol
 chalcone
 1 mol

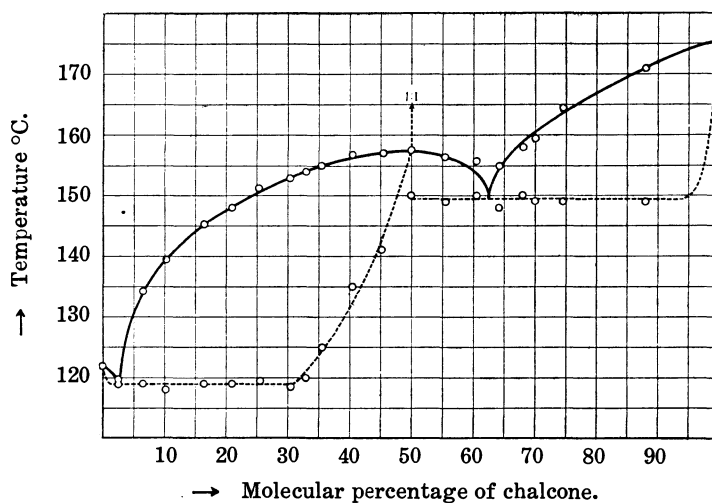


Fig. 4.

The system : 4'-Ethoxybenzalacetophenone—
picric acid (See Fig. 5)

Molecular percentages of		Temperatures of	
Chalcone	Picric acid	Thawing	Complete fusion
0.0	100.0	—	122.0
4.6	95.4	82.5	118.5
9.2	90.8	81.5	116.0
13.8	86.2	81.5	112.0
18.5	81.5	79.5	110.0
23.2	76.8	81.0	106.3
28.0	72.0	79.5	—
32.8	67.2	81.3	98.0
37.4	62.6	80.4	93.0
37.7	62.3	81.0	—
40.0	60.0	80.0	89.0
42.6	57.4	81.0	—
44.6	55.4	80.0	85.0
47.1	52.9	81.0	83.0
48.0	52.0	80.5	82.5
49.7	50.3	80.5	84.0
50.7	49.3	75.0	—
57.6	42.4	65.0	83.2
68.0	32.0	60.5	79.0
78.4	21.6	61.0	69.5
89.2	10.8	62.0	68.5
93.5	6.5	65.0	72.0
100.0	0.0	73.5	74.5

Eutectic points :

81.0°C. picric acid
53.5 mol %
60.5°C. picric acid
16.7 mol %

Distectic point :

84.5°C. { picric acid 1 mol
chalcone 1 mol

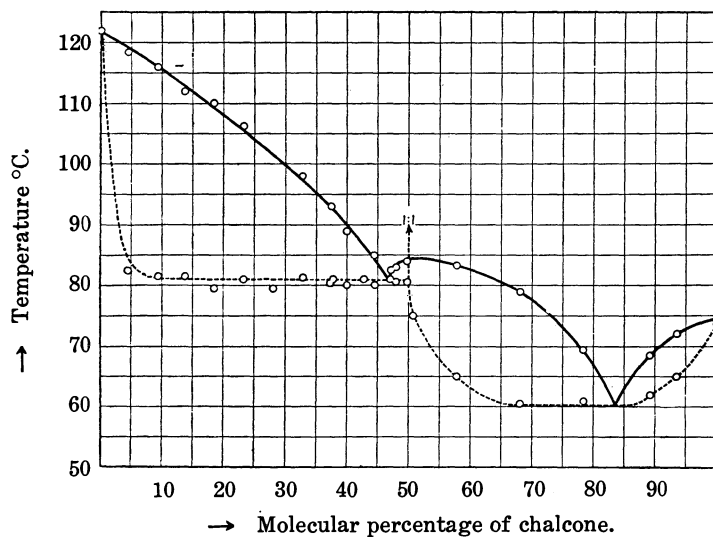


Fig. 5.

The system : 3,4-Methylenedioxybenzal-
acetophenone— β -naphthol (See Fig. 6)

Molecular percentages of		Temperatures of	
Chalcone	β -Naphthol	Thawing	Complete fusion
0.0	100.0	—	121.5
6.3	93.7	72.0	116.5
12.5	87.5	72.0	111.5
19.7	80.3	71.0	104.5
27.6	72.4	72.0	95.5
36.4	63.6	71.0	83.8
46.1	53.9	71.0	80.0
57.2	42.8	71.0	95.5
63.2	36.8	71.5	100.5
69.6	30.4	71.0	106.6
76.4	23.6	72.0	110.8
83.8	16.2	71.5	114.5
91.6	8.4	72.0	118.4
100.0	0.0	—	121.0

Eutectic point :
71.5°C. β -naphthol
58.2 mol %

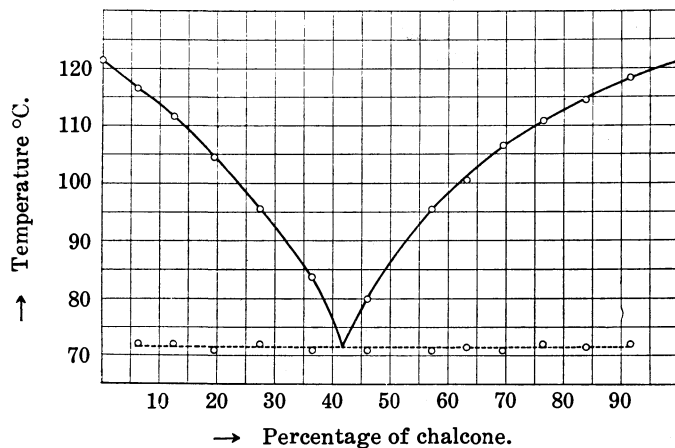


Fig. 6.

In conclusion, the author wishes to express his best gratitude to Prof. Y. Shibata for his kind and at the same time useful advises throughout this research.

HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. VII.

By Susumu MIYAMOTO.

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Investigations of the reduction of a number of inorganic solid substances by hydrogen in the silent electric discharge have been carried out over a considerable period; there follows an account of the results obtained since the publication of the previous papers.⁽¹⁾

The apparatus and method of investigation are the same as those previously mentioned.⁽¹⁾

Experimental.

(1) **Lithium Nitrate.** A gas absorption apparatus similar to that employed in the case of calcium nitrate⁽²⁾ was connected to the apparatus. Nitrogen peroxide contained in the gaseous reaction products is absorbed by alkaline solution in absorption bottle (1), nitric oxide is then oxidized by air and absorbed by alkaline solution in absorption bottle (2), and, lastly, ammonia gas is absorbed by dilute sulphuric acid solution in absorption bottle (3).

Exp. 1. A qualitative experiment was first carried out.

The quantity of lithium nitrate, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Water was produced during the reaction and part of the powder in the discharge tube became moist.

Distilled water was added into the discharge tube and the chemical properties of the solution produced were examined, with the following results:—

- (a) The solution was basic. It coloured red litmus paper blue.
- (b) On adding silver nitrate solution, a chocolate-brown precipitate of silver oxide was produced.
- (c) The solution was neutralized with nitric acid solution and silver nitrate solution added. No yellow precipitate was obtained, proving the absence of hyponitrite.

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202.

(2) S. Miyamoto, *ibid.*, **54** (1933), 89.

- (d) The solution was added to Fehling's solution and heated. No reduction took place, proving the absence of hydroxylamine.
- (e) The solution was placed in a test tube, potassium iodide solution added, acidified with dilute sulphuric acid solution and a few drops of starch solution added. The solution was coloured blue, proving the presence of nitrite.
- (f) The solution was placed in a test tube and heated. Moist red litmus paper became blue, proving the evolution of ammonia.

The alkaline solution in absorption bottle (1) was placed in a test tube, potassium iodide solution added, acidified with dilute sulphuric acid solution and a few drops of starch solution added. The solution was coloured slightly blue, proving that a minute quantity of nitrogen peroxide had been produced during the reaction.

By analyzing the alkaline solution in absorption bottle (2) it was proved that nitric oxide is not a gaseous reaction product.

The sulphuric acid solution in absorption bottle (3) was placed in a test tube, alkalinized with sodium hydroxide solution and heated. The evolution of ammonia gas was proved.

Exp. 2. The solid reaction product was dissolved in water and the total volume of the solution was made up to 100 c.c. The quantity of nitrite was determined in the normal manner.

Lithium nitrate employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.10 c.c.

Exp. 3. The solid reaction product was dissolved in dilute nitric acid solution, and distilled with an excess of sodium hydroxide solution. The ammonia gas evolved was absorbed by a definite quantity of sulphuric acid solution. The distillation was stopped when no further evolution of ammonia took place, and the excess of sulphuric acid was titrated with sodium carbonate solution.

The quantity of ammonia gas absorbed by sulphuric acid solution in absorption bottle (3) during the reaction was similarly determined.

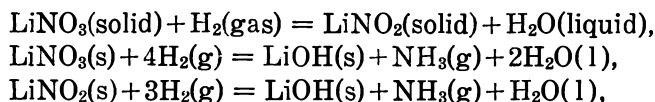
Lithium nitrate employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia evolved when the solid reaction product was distilled with an excess of sodium hydroxide solution = 0.24 c.c.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed by sulphuric acid solution in absorption bottle (3) = 0.29 c.c.

From these experimental facts, it would seem that the principal chemical reactions in the discharge tube are expressed by the following equations.



(2) **Beryllium Nitrate.** Exp. 1. The quantity of beryllium nitrate, $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, employed = 8.00 gr. Time of silent electric discharge = 5 hours.

A gas absorption apparatus similar to that employed in the previous case was connected to the discharge tube.

Soon after the electric current was passed, a considerable quantity of brown coloured gas, which is undoubtedly nitrogen peroxide, evolved in the discharge tube. Water was found condensed on the wall of the discharge tube.

Water was poured into the discharge tube, well shaken and filtered. A small quantity of insoluble white powder remained. It was filtered and washed. The insoluble white powder is undoubtedly beryllium hydroxide. The filtrate had the following chemical properties.

- (a) The solution was acidic. This is due to the hydrolysis of beryllium nitrate unchanged.
- (b) By the identical method employed in the previous case, it was proved that the solution contained nitrite. As beryllium nitrite is unknown, the nitrite contained in the solution is supposed to be ammonium nitrite produced during the reaction.
- (c) The presence of ammonium salt was proved.
- (d) The absence of hydroxylamine was proved in the normal manner.

Exactly as in the case of lithium nitrate, it was proved that the gaseous reaction products contained no ammonia gas but considerable quantities of nitrogen peroxide and nitric oxide.

Exp. 2. The quantity of ammonium salt produced was determined in the normal manner.⁽³⁾

Beryllium nitrate employed = 8.00 gr.

Time of silent electric discharge = 5.5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 8.47 c.c.

Exp. 3. The quantities of nitrite, nitrogen peroxide and nitric oxide produced were determined.

(3) Treadwell, "Kurztes Lehrbuch der analytischen Chemie," 10. Aufl., 2. Bd., S. 483.

On leaving the discharge tube, the gas was first passed through two absorption bottles containing sodium hydroxide solution (a), the gas was then mixed with a sufficient quantity of air and passed through two absorption bottles containing sodium hydroxide solution (b).

The quantity of nitrite contained in the solid reaction products was determined in the normal manner.

Beryllium nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

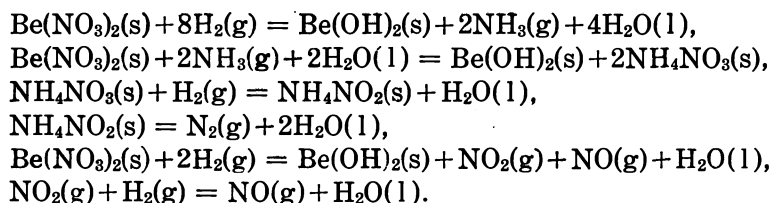
Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced in the solid phase = 2.80 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottle (a) formed by absorbing nitrogen peroxide = 249.40 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottle (b) formed by absorbing nitrogen peroxide, which is the oxidation product of nitric oxide, produced during the reaction = 522.20 c.c.

From these experimental facts, it is certain that the principal reaction products are beryllium hydroxide, nitrite, ammonium salt, nitrogen peroxide and nitric oxide. It is a notable fact that the quantities of nitrogen peroxide and nitric oxide produced in this case are considerable compared with those produced in the case of nitrates of other metals, such as magnesium,⁽⁴⁾ zinc,⁽⁵⁾ cadmium,⁽⁶⁾ calcium,⁽⁷⁾ strontium⁽⁸⁾ and barium.⁽⁹⁾

It is probable that the principal chemical reactions in the discharge tube are expressed by the following equations.



(3) **Mercuric Nitrate.** The investigation of the reduction of mercuric nitrate was repeated to supplement the previous study.⁽¹⁰⁾

Exp. 1. The quantity of mercuric nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, employed = 8.00 gr.
Time of silent electric discharge = 6 hours.

(4) S. Miyamoto, *J. Chem. Soc. Japan*, **54** (1933), 209.

(5) *Ibid.*, **54** (1933), 210. (6) *Ibid.*, **54** (1933), 211.

(7) *Ibid.*, **54** (1933), 89. (8) *Ibid.*, **54** (1933), 91.

(9) *Ibid.*, **54** (1933), 92. (10) *Ibid.*, **53** (1932), 942.

A gas absorption apparatus similar to that employed in the case of lithium nitrate was connected to the discharge tube.

Virtually no change was observed in the appearance of the powder in the discharge tube.

The solid reaction product was first examined and it was proved that it contained no explosive compounds. The solid reaction product was then shaken with water and filtered. An insoluble yellow powder remained, which is undoubtedly mercuric oxide. The filtrate had the following properties.

- (a) The solution was acidic.
- (b) A sufficient quantity of sodium hydroxide solution was added to the solution and the precipitated mercury oxide filtered. The filtrate contained no hydroxylamine.
- (c) The solution contained nitrite. The quantity of nitrite produced was determined in the previous study.⁽¹⁰⁾
- (d) Exactly as in the case of beryllium nitrate, it was proved that the solution contained a considerable quantity of ammonium salt.
- (e) It was proved that the solution contained mercurous salt. The quantity of mercurous salt produced was determined in the previous study.⁽¹⁰⁾

Exactly as in the case of lithium nitrate it was proved that the gaseous reaction products contained neither ammonia nor nitric oxide, but nitrogen peroxide.

The quantity of nitrogen peroxide produced was determined in the previous experiment.⁽¹⁰⁾

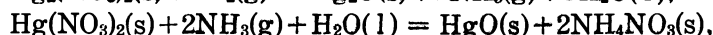
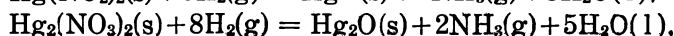
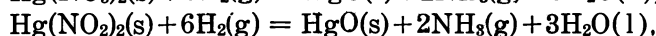
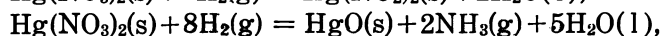
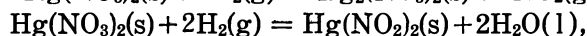
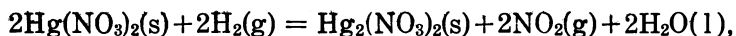
Exp. 2. The solid reaction products were dissolved in dilute nitric acid solution and the quantity of ammonium salt was determined in the normal manner.

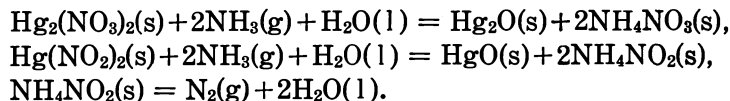
Mercuric nitrate employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 12.13 c.c.

From these experimental facts it would seem that the principal chemical reactions in the discharge tube are expressed by the following equations.





(4) **Mercurous Nitrate.** This investigation of the reduction of mercurous nitrate was carried out to supplement the previous study.⁽¹¹⁾

Exp. 1. The quantity of mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, employed = 8.00 gr.
Time of silent electric discharge = 5 hours.

The white powder in the discharge tube became grey in colour. The solid reaction products were shaken with water. An insoluble white powder and small drops of metallic mercury remained. The quantity of metallic mercury was determined in the previous study. The solution had the following chemical properties.

- (a) The solution was acidic.
- (b) The solution contained ammonium salt.
- (c) The solution contained nitrite. The quantity of the produced nitrite was determined in the previous study.
- (d) Sodium hydroxide was added to the solution and the precipitated mercury oxide filtered. The absence of hydroxylamine in the filtrate was proved.

By analyzing the alkaline solutions in absorption bottles (1) and (2) it was proved that nitrogen peroxide and a minute quantity of nitric oxide had been produced during the reaction.

By analyzing the sulphuric acid solution in absorption bottle (3) it was proved that the gaseous reaction products contained no ammonia.

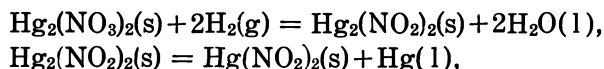
Exp. 2. The production of ammonium salt was studied quantitatively. The solid reaction products were well shaken with dilute nitric acid solution, and the drops of metallic mercury were separated by decantation. The quantity of ammonium salt contained in the solution was determined in the normal manner.

Mercurous nitrate employed = 8.00 gr.

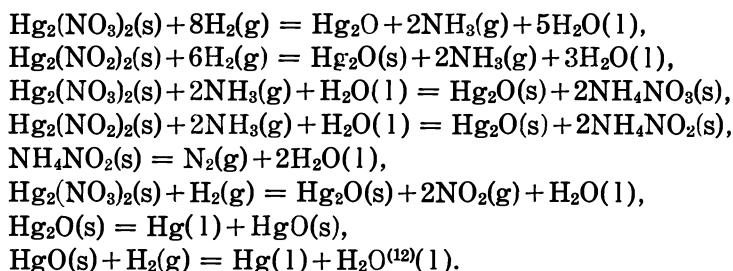
Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 9.48 c.c.

From these results the principal reactions in the discharge tube are considered to be those expressed by the following equations.



(11) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 943.



(5) **Lead Nitrate.** Exp. 1. The quantity of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, employed = 8.00 gr. Time of silent electric discharge = 5 hours.

A gas absorption apparatus similar to that employed in the previous experiment was connected to the discharge tube. A part of the white powder in the discharge tube became black. It was first proved that the solid reaction product did not contain any explosive compound. The powder was then shaken with water and filtered. A small quantity of white powder mixed with a minute quantity of black powder remained. It is certain that the insoluble substance is a mixture of lead hydroxide and metallic lead. The filtrate had the following properties.

- (a) The solution coloured red litmus paper slightly blue.
- (b) Sodium carbonate solution was added to the solution and the precipitated lead carbonate filtered. The absence of hydroxylamine in the filtrate was proved.
- (c) The presence of nitrite in the solution was proved.
- (d) The solution contained ammonium salt.

It was proved that the gaseous reaction products contained a small quantity of nitrogen peroxide and ammonia, but no nitric oxide.

Exp. 2. The formation of nitrite was studied quantitatively.

Lead nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 3.80 c.c.

Exp. 3. The quantity of ammonium salt contained in the solid reaction product was determined.

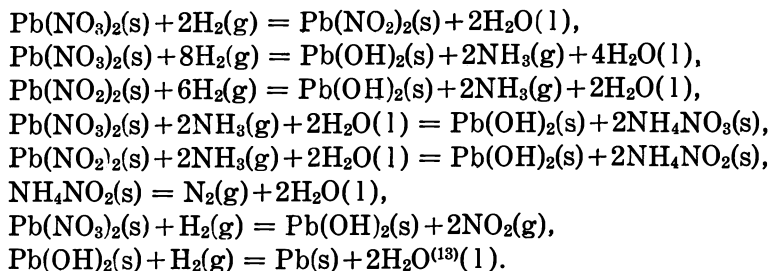
Lead nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 0.85 c.c.

(12) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 793.

From these experimental facts, it would seem that the principal reactions are expressed by the following equations.



(6) **Bismuth Nitrate.** Exp. 1. The quantity of bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, employed = 8.00 gr. Time of silent electric discharge = 5 hours.

Soon after the electric current had been passed, a considerable quantity of brown coloured gas, undoubtedly nitrogen peroxide, evolved in the discharge tube. A part of the powder in the discharge tube became black. A minute quantity of metallic bismuth must have been produced. The solid reaction product was shaken with water. A small quantity of insoluble white substance remained: this is undoubtedly bismuth hydroxide. The insoluble matter was filtered. The filtrate had the following properties.

- (a) The solution was acidic.
- (b) The solution contained ammonium salt.
- (c) The presence of nitrite was proved.
- (d) It was proved that the solution contained no hydroxylamine.

By analyzing the solutions in absorption bottles (1), (2) and (3), it was proved that the gaseous reaction products contained nitrogen peroxide and nitric oxide, but no ammonia gas.

Exp. 2. The quantities of nitrite, nitrogen peroxide and nitric oxide produced were determined by the method employed in the case of beryllium nitrate.

Bismuth nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.0100 normal, equivalent to the quantity of nitrite produced in the solid phase = 5.45 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottles (1), produced by absorbing nitrogen peroxide = 569.80 c.c.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite in absorption bottles (2), produced by absorb-

(13) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 794.

ing nitrogen peroxide, the oxidation product of nitric oxide, a gaseous reaction product = 811.30 c.c.

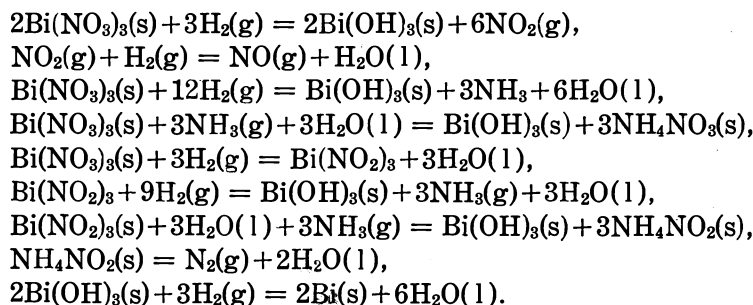
Exp. 3. The quantity of ammonium salt produced was determined.

Bismuth nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 1.88 c.c.

From these experimental facts, it would seem that the principal chemical reactions are expressed by the following equations.



As in the case of beryllium nitrate, the quantities of nitrogen peroxide and nitric oxide contained in the gaseous reaction products were considerable.

(7) **Aluminium Nitrate.** Exp. 1. The quantity of aluminium nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, employed = 8.00 gr. Time of silent electric discharge = 5 hours.

The powder in the discharge tube became moist owing to the formation of water by the reduction. Distilled water was poured into the discharge tube, well shaken, and filtered. A minute quantity of white powder remained. The powder was placed in a test tube, dilute hydrochloric acid solution added and warmed. It dissolved, forming aluminium chloride solution. It is therefore certain that the white powder, insoluble in water, is aluminium oxide. The filtrate had the following properties.

- (a) The solution was acidic. This is due to the presence of unchanged aluminium nitrate.
- (b) It was proved that the solution contained nitrite. As aluminium nitrite is unknown, it would seem that the produced nitrite must be ammonium nitrite, formed by the reaction.
- (c) The solution contained ammonium salt.
- (d) The solution contained no hydroxylamine.

By a method similar to that employed in the case of lithium nitrate it was proved that the gaseous reaction products contained neither nitric oxide nor ammonia gas, but nitrogen peroxide.

Exp. 2. A second experiment was carried out to determine the quantity of ammonium salt produced.

Aluminium nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 10.34 c.c.

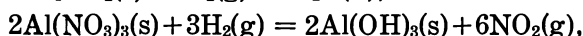
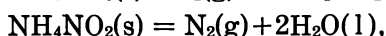
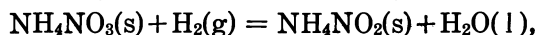
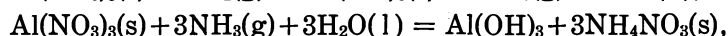
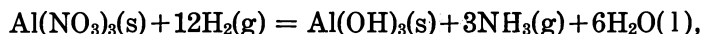
Exp. 3. The quantity of nitrite, contained in the solid reaction products, was determined in the normal manner.

Aluminium nitrate employed = 8.00 gr.

Time of silent electric discharge = 4.5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.15 c.c.

From these experimentally obtained facts it follows that the principal reaction products are ammonium salt, aluminium hydroxide, nitrite and nitrogen peroxide, and it would seem that the chemical reactions are expressed by the following equations.



(8) **Ammonium Nitrate.** Exp. 1. The quantity of ammonium nitrate, NH_4NO_3 , employed = 8.00 gr. Time of silent electric discharge = 5 hours.

A gas absorption apparatus, similar to that employed in the previous experiment was connected to the discharge tube. Virtually no change was observed in the appearance of the powder in the discharge tube. The solid reaction products were dissolved in water. The solution had the following properties.

(a) The solution was neutral.

(b) The solution contained no hydroxylamine.

(c) The solution contained a minute quantity of nitrite.

It was proved that the gaseous reaction products contained ammonia and a minute quantity of nitrogen peroxide, but no nitric oxide.

Exp. 2. The nitrite and the ammonia gas produced were determined quantitatively.

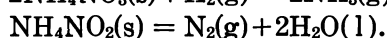
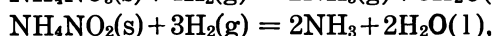
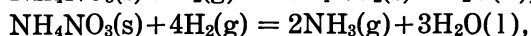
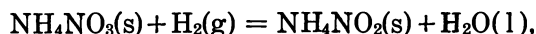
Ammonium nitrite employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 0.10 c.c.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia gas evolved = 0.29 c.c.

From these experimental facts it would seem that the chemical reactions are those expressed by the following equations.



The writer wishes to express his appreciation of a grant from the Imperial Academy towards the expences of this research.

Summary.

The chemical reactions in the silent electric discharge were studied when hydrogen reacts on the following inorganic solid substances.

(1) Lithium nitrate. Reaction products:—lithium hydroxide, nitrite, ammonia and nitrogen peroxide.

(2) Beryllium nitrate. Reaction products:—beryllium hydroxide, ammonium salt, nitrite, nitrogen peroxide and nitric oxide.

(3) Mercuric nitrate. Reaction products:—mercury oxide, mercurous salt, ammonium salt, nitrite and nitrogen peroxide.

(4) Mercurous nitrate. Reaction products:—mercury oxide, metallic mercury, ammonium salt, nitrite, nitrogen peroxide and nitric oxide.

(5) Lead nitrate. Reaction products:—lead hydroxide, ammonium salt, nitrite, (metallic lead), nitrogen peroxide and ammonia.

(6) Bismuth nitrate. Reaction products:—bismuth hydroxide, ammonium salt, nitrite, (metallic bismuth), nitrogen peroxide and nitric oxide.

(7) Aluminium nitrate. Reaction products:—aluminium oxide, ammonium salt, nitrite and nitrogen peroxide.

(8) Ammonium nitrate. Reaction products:—nitrite, ammonia and nitrogen peroxide.

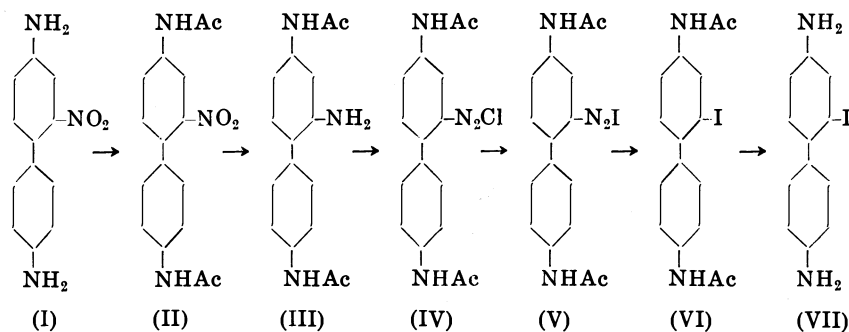
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SOME DERIVATIVES OF BENZIDINE.

By Shin-ichi SAKO.

Received November 20th, 1933. Published March 28th, 1934.

In connection with another work it became necessary to prepare 2-iodobenzidine (VII). Starting from 2-nitrobenzidine which could easily be produced by Täuber's method⁽¹⁾ the substance (VII) was obtained by the following series of processes :



As is to be expected, the difficulty encountered in this series of reactions arose from the ease with which the acetamido-groups were hydrolysed by the action of acids. On this account, the reduction of the nitro-compound (II) had to be carried out with a solution of stannous chloride and dry hydrogen chloride in glacial acetic acid. Similarly, in the production of the iodo-compound (VI) from the diazonium iodide (V), which was deposited in a stable crystalline form at ordinary temperature, the decomposition of (V) must not be effected in the usual way, that is, by heating in the presence of water. Fortunately, this difficulty could be got over by treating the solid diazonium iodide (V) with glacial acetic acid, when the decomposition took place even in the cold giving rise to the iodo-compound (VI) in an excellent yield.

It has been found that 2-nitrobenzidine exists in two forms, one recorded by Täuber having m.p. 143°C. and the other described in this paper m.p. 117°C. The detailed account of this discovery will be given in the experimental part, but a fact which deserves mention was that, although the author at first could prepare the lower melting form only, as

(1) *Ber.*, **23** (1890), 796.

soon as the higher melting form had once been produced, it was then the turn of the labile form which could no longer be obtained, a phenomenon which recalls the similar case in Liebermann's iso-cinnamic acid (m.p. 58°C.) which, when more stable allo-cinnamic acid (m.p. 68°C.) had been obtained, could be produced no more in his laboratory.⁽²⁾

It was found that 2-aminobenzidine obtainable by the reduction of 2-nitrobenzidine (I) also exhibits dimorphism, the melting point, 134°C. described by Täuber being that of the more stable form. As in the case of 2-nitrobenzidine, the less stable form having m.p. 50°C. was the first to be obtained, its conversion into the more stable form being easily accomplished. Unlike 2-nitrobenzidine, the labile form could be obtained even after the stable form had been produced.

Experimental.

2-Nitrobenzidine (I). The more stable form of this compound was obtained by the action of ammonia on the 2-nitrobenzidine sulphate which was produced by treating a solution of the benzidine sulphate in concentrated sulphuric acid with potassium nitrate.⁽¹⁾ Later Le Fèvre and Turner⁽³⁾ found that in the nitration of benzidine the same result could be obtained by the use of the free base in place of the sulphate. The less stable form, the production of which was not observed by these workers, was found to be deposited when, for instance, a solution of the 2-nitrobenzidine sulphate (3.0 gr.) in boiling water (600 c.c.) was treated with a 20 per cent. ammonium hydroxide solution (7 c.c.). Some time after the addition of ammonia, the free base separated as an oil which, on being scratched, formed deep red, long needles which to the author's surprise melted, not at 143°C. as described by Täuber, but sharply at 117°C. As a matter of course, many attempts to prepare the higher melting form were made, which however led to no purpose for about a fortnight. Meanwhile, it was discovered that a slight but perceptible discoloration occurred in some of the crystals which had been put in a desiccator for some days. On examination, these crystals were found to melt at 143°C., showing that the conversion of the lower melting form into the higher had taken place. As to the remarkable phenomenon that the labile form was incapable of existence after the production of the stable form, it has already been stated in the introduction. Although both forms resembled chromic acid both in colour and in the crystalline form, there were still distinguishable difference

(2) *Ber.*, **23** (1890), 141, 2510.

(3) *J. Chem. Soc.*, **1926**, 1762.

between their appearances, the needles of the labile form being longer and having deeper colour than those of the more stable form. Both forms gave the same diacetyl compound.

2-Aminobenzidine. This compound was obtained by Täuber⁽¹⁾ by the reduction of 2-nitrobenzidine (I) with tin and hydrochloric acid. The author employed stannous chloride in place of tin. After the removal of tin from the reaction mixture by the use of hydrogen sulphide, the filtrate was greatly concentrated, when the trihydrochloride separated in transparent crystals. It was purified by treating with animal charcoal and the salt precipitated by the addition of concentrated hydrochloric acid to the concentrated filtrate.

As stated in the introduction, 2-aminobenzidine exists in two forms, one having m.p. 134°C. and the other 50°C. The former was obtained by Täuber.⁽¹⁾ The latter was produced as follows: when conc. ammonia (25 c.c.; $D = 0.89$) was added to a solution of the trihydrochloride (1.0 gr.) in water (15 c.c.) no precipitation occurred, but upon filtering the solution long needles separated after a short time, which melted at 50°C. A more concentrated solution of the salt than that employed above, on treatment with ammonia immediately deposited the base as an oil which crystallized only after being left for a long time. At first, attempts to obtain the more stable form was not successful, the labile form remaining unchanged even on being heated above its melting point. But this change could be effected afterwards by the same treatment.

2-Amino-NN'-diacetylbenzidine (III). 2-Nitrodiacetyl benzidine (II), from which 2-aminodiacyl benzidine (III) was obtained, was prepared by a modification of the method of Le Fèvre and Turner⁽³⁾: a solution of 2-nitrobenzidine (30 gr.) in glacial acetic acid (90 c.c.) was treated with acetic anhydride (30 c.c.). A short time later, the diacetyl compound commenced to separate. After heating the mixture on the water bath for an hour it was allowed to cool and the product collected and washed with acetic acid. The yield was 41.0 gr. (quantitative). Treatments such as described by Le Fèvre and Turner, that is, the addition of water to the reaction mixture before the filtration of the product and also the extraction of the product with methylated spirit are not necessary. 2-Nitrodiacetylbenzidine thus obtained melted, with darkening and previous sintering, at 317°C.

Attempted reduction of 2-nitrodiacetyl benzidine for the preparation of the 2-aminodiacyl benzidine with iron and acetic acid or with aluminium amalgam and aqueous alcohol failed. The reduction was, however, successfully accomplished as follows: 2-nitro-NN'-diacetylbenzidine (50.0 gr.) was added with constant shaking to a cold solution which was prepared by

saturating dry hydrogen chloride in a mixture of stannous chloride (130.0 gr.) and glacial acetic acid (600 c.c.). The nitro-compound gradually disappeared with a rise of temperature up to 50–60°C. The reduction product began to separate after half an hour or so from the start, when there still remained some original substance unattacked. It was necessary for the complete disappearance of the nitro-compound to shake the mixture for two hours during which hydrogen chloride was led in all the time. After that, the mixture was heated in a water bath at 40°C. for an hour and left over night. The double chloride thus separated was dried over soda lime under diminished pressure. The yield was 97.5 gr.

The powdered double salt (15.0 gr.) obtained above was added in small portions to 2000 c.c. of cold water with efficient agitation which was continued until the substance had completely dissolved (In mixing these two substances the above order should not be reversed, as, if water is added to the double chloride, it is apt to cake together, making its dissolution more difficult. Further, the dissolution must not be effected by heating, as this may cause the hydrolysis of the acetamido-groups). The disappearance of the original substance was followed by the separation of a white precipitate, probably a basic salt of tin, which increased in amount when hydrogen sulphide was passed into the mixture. All of tin present was thus precipitated mostly as the white precipitate and partly as the yellow sulphide. The clear filtrate separated from the precipitates, on treatment with a solution of crystalline sodium acetate (25.0 gr.), quickly deposited 2-amino-diacetyl benzidine (III) as white powder which was filtered after a time. The yield was over 80% of the theoretical, calculated on the 2-nitrodiacetyl benzidine employed. The 2-aminodiacetyl benzidine thus obtained was pure enough for further experiment as indicated by its melting point (260–262°C.). For purification, 0.24 gr. of the substance was dissolved in about 600 c.c. of boiling water and the solution concentrated until its bulk reached 200 c.c. On cooling, light, lustrous crystals (0.23 gr.) melting at 261–262°C. was obtained (Found : N = 15.1%. $C_{16}H_{17}O_2N_2$ requires N = 14.8%).

2-Iodo-NN'-diacetylbenzidine (VI). An ice cold, 15 per cent. hydrochloric acid solution (90 c.c.) was well mixed with powdered 2-aminodiacetyl benzidine (15.0 gr.). The pasty mass thus obtained after the addition of cold water (40 c.c.), was treated, with cooling by ice, with powdered sodium nitrite (3.8 gr.) in small portions at a time with mechanical agitation. After half an hour, a solution of potassium iodide (10.5 gr.) was added to the reaction mixture, when the diazonium iodide (V) separated as a brownish-red precipitate which did not decompose unless heated at a fairly high temperature. As however it was found that the heating of diazonium iodide

suspended in the reaction mixture caused at the same time the hydrolysis of the acetamido-groups, it was filtered off after 30 minutes from the addition of potassium iodide, pressed and without washing with water (for it is more or less soluble in fresh water.), added to cold glacial acetic acid (200 c.c.). The decomposition set in at once with copious evolution of gas, 2-iododiacetyl bezidine separating as a yellow precipitate which was collected and washed with acetic acid. The dried crude product, 16.1 gr., was redissolved in boiling acetic acid (1000 c.c.) and treated with animal charcoal. The clear filtrate was concentrated until the liquid had one-third the original bulk, when the crystals began to appear. Yellow short needles thus obtained (13.4 gr.) had m.p. 310–311°C. (Found: N = 7.4%. $C_{16}H_{15}O_2N_2I$ requires N = 7.1%).

Dihydrochloride of 2-Iodobenzidine. A suspension of 2-iododiacetyl benzidine (10.0 gr.) in conc. HCl (25 c.c.) and ethyl alcohol (100 c.c.) was heated under reflux on the water bath for two hours with occasional shaking. The disappearance of the original substance for which one hour's heating was necessary was followed by the gradual separation of the dihydrochloride of 2-iodobenzidine in small needles. After requisite time, it was cooled and the reddish yellow crystals collected and washed with ethyl alcohol. The yield was 9.3 gr. (Found: HCl = 18.7; N = 7.3%. $C_{13}H_{11}N_2I \cdot 2HCl$ requires HCl = 19.0; N = 7.3%).

Sulphate of 2-Iodobenzidine. 2-Iiododiacetyl benzidine (3.1 gr.) suspended in ethyl alcohol (30 c.c.), conc. H_2SO_4 (3 c.c.), and water (9 c.c.) was heated at 100°C. for 5 hours. Most of the original substance disappeared in two hours. A small trace of the insoluble matter was removed by means of hot filter. The filtrate, on being left over night, gave 2.7 gr. of the crystalline sulphate of 2-iodobenzidine (Found: H_2SO_4 = 23.6%. $C_{12}H_{11}N_2I \cdot H_2SO_4$ requires H_2SO_4 = 24.0%).

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. IX.

By Tetsuya ISHIKAWA.

Received March 5th, 1934. Published April 28th, 1934.

The viscosity of binary mixtures of partially miscible liquids has been little studied. Chadwell and his coworker⁽¹⁾ made careful determinations of viscosities at 10° and 25°C. of methyl acetate, ethyl acetate and ethyl ether in water, all of which display greater viscosities than the component viscosities—similar phenomena to the water solutions of methyl alcohol, ethyl alcohol, or acetic acid. They believed that the solvation might be the most plausible explanation for these cases, but gave no confirmation of the compound formation, probably with the reason that from these viscosity curves only no tracing could be made up to the points of maxima which roughly determine the composition of the molecular compounds in solution.

Howell⁽²⁾ studied the system of phenol and water, the viscosity-concentration curves of which are sagged at all the temperatures below the critical solution temperature (66.4°C.), but with somewhat complex nature at 70°C. He noticed that the deviation maximum of the measured viscosities from those calculated from his adopted mixture law (linear in weight fraction) corresponded approximately to a compound of equimolecular proportion of phenol and water, and that from the sagged property of the viscosity curves the hydrate might partially dissociate in the manner: $C_6H_5OH + H_2O \rightleftharpoons C_6H_5OH.H_2O \rightleftharpoons C_6H_5O' + OH_3$, but reported in his second communication⁽³⁾ that the electrical conductivity at this phenol rich solution showed an extremely low value. This fact necessitated another suitable explanation. Thus, he assumed that at phenol rich solutions the other form of the ionic dissociation, $C_6H_5OH + H_2O \rightleftharpoons C_6H_5OH_2 + OH'$, might occur and that this ionization might be the least at the equimolecular proportion of phenol and water to form a molecular compound $C_6H_5OH.H_2O$. Before accepting his hypotheses, however, one

(1) H. M. Chadwell, *J. Am. Chem. Soc.*, **48** (1926), 1912; H. M. Chadwell & B. Asnes, *J. Am. Chem. Soc.*, **52** (1930), 3507.

(2) O. R. Howell, *Trans. Farad. Soc.*, **28** (1932), 912.

(3) O. R. Howell & C. Handford, *Trans. Farad. Soc.*, **29** (1933), 640.

must doubt the adaptability of the mixture law taken by him for calculating the deviation from the observed viscosity values.

The writer⁽⁴⁾ has recently developed the solvation viscosity in the following form:

$$\delta = \eta - \eta_0 = C_0(\eta_1^{\nu_1}\eta_2^{\nu_2})^{\frac{m}{\nu_1+\nu_2}}(1-z_m)^{\nu_1}z_m^{\nu_2},$$

where δ is the solvation viscosity which is the difference of the measured viscosity η from that calculated from his formula for an ideal mixture η_0 ; η_1 and η_2 the viscosities of components 1 and 2; ν_1 and ν_2 the numbers of molecules of components 1 and 2 taking into chemical reaction to form a molecular compound; z_m the formal molar fraction of component 2; C_0 and m the constants independent of the temperature and concentration so long as the molecular compound exists in the concentration range, m which is termed by the stability coefficient being a numerical measure of the stability of the molecular compound.

The present paper is a study on binary mixtures of partially miscible liquids from the same standpoint of view. The viscosity values of the water solutions of ethyl acetate and of ethyl ether are quoted from Chadwell's data and those of phenol and water are from Howell's observations.

For the first two pairs the quotients $\frac{k_2a_2}{k_1a_1}$ at so near temperatures as 10° and 25°C. are regarded to be quite equal and the following values at 25°C. already obtained⁽⁵⁾ will be used:

For the water (1) and ethyl acetate (2) mixture, $\frac{k_2a_2}{k_1a_1} = \frac{1.64 \times 1.25}{0.21 \times 3.18} = 3.07$; and for the water (1) and ethyl ether (2) mixture, $\frac{k_2a_2}{k_1a_1} = \frac{3.09}{0.21 \times 3.18} = 4.63$, the numerator being the mean value of $k_2a_2 = 3.03$ and 3.15 calculated from the two mixtures of ethyl ether and ethyl alcohol and of ethyl ether and propyl alcohol which were discussed in part IV.⁽⁶⁾ For the system of water and phenol the quotient previously obtained at 20°C. may not be applicable to higher temperatures simply considering that the boiling points of these liquids differ much from each other. In fact, as table 1 shows, the quotients $\left(\frac{k_2a_2}{k_1a_1}\right)_z$ at the same concentration have different values at 50°, 60° and 70°C. By trial, the re-

(4) This Bulletin, **8** (1933), 280.

(5) This Bulletin, **4** (1929), 25.

(6) This Bulletin, **4** (1933), 288.

ciprocals of these quotients at each temperature are found to be linear, from whose relationship the extrapolated values at $z=1$ can be easily estimated provided that the degree of association of water molecules undergo no change at infinite dilution with phenol. In column 7 in table 1 are shown the quotients thus obtained. The values in brackets denote the required quotients $\frac{k_2 a_2}{k_1 a_1} = \left(\frac{k_2 a_2}{k_1 a_1} \right)_z \frac{M_2}{M_1}$, M_1 and M_2 being the molecular weights of water and phenol respectively.

Table 1.

H₂O—C₆H₅OH (Howell).

z -C ₆ H ₅ OH	0.70	0.75	0.80	0.85	0.90	0.95	1.00
$\left(\frac{k_2 a_2}{k_1 a_1} \right)_z \begin{cases} 50^\circ \\ 60^\circ \\ 70^\circ \end{cases}$	0.306	0.267	0.239	0.215	0.194	0.178	0.165 (0.86)
	0.337	0.299	0.274	0.249	0.227	0.207	0.194 (1.01)
	0.369	0.331	0.305	0.283	0.263	0.239	0.225 (1.17)

Table 2.

H₂O—CH₃COOC₂H₅, 10°C. (Chadwell & Asnes).

z -CH ₃ COOC ₂ H ₅	z_m -CH ₃ COOC ₂ H ₅	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.013105	—	—	—
0.00522	0.00107	0.013230	0.013079	0.000151	(0.141)
0.02613	0.00547	0.014178	0.012972	0.001206	0.222
0.02845	0.00597	0.014242	0.012960	0.001282	0.216
0.03206	0.00673	0.014456	0.012942	0.001514	0.226
0.04804	0.01022	0.015117	0.012859	0.002258	0.223
0.06683	0.01444	0.015968	0.012760	0.003208	0.225
1.00000	1.00000	0.005092	—	—	—
					mean 0.222

25°C. (Chadwell).

z -CH ₃ COOC ₂ H ₅	z_m -CH ₃ COOC ₂ H ₅	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.008949	—	—	—
0.00676	0.00139	0.009095	0.008929	0.000166	0.120
0.00892	0.00184	0.009129	0.008923	0.000206	0.112
0.01815	0.00377	0.009354	0.008895	0.000459	0.122
0.03041	0.00638	0.009652	0.008858	0.000794	0.125
0.03284	0.00690	0.009678	0.008851	0.000827	0.121
0.04809	0.01023	0.010043	0.008804	0.001239	0.122
0.06170	0.01328	0.010357	0.008762	0.001595	0.122
1.00000	1.00000	0.004244	—	—	—
					mean 0.121

Table 3.
 $\text{H}_2\text{O}-(\text{C}_2\text{H}_5)_2\text{O}$, 10°C . (Chadwell & Asnes).

$z-(\text{C}_2\text{H}_5)_2\text{O}$	$z_m-(\text{C}_2\text{H}_5)_2\text{O}$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.013105	—		
0.01031	0.00253	0.013640	0.012983	0.000657	0.261
0.01408	0.00346	0.013870	0.012939	0.000931	0.270
0.02894	0.00720	0.014747	0.012764	0.001983	0.277
0.05751	0.01462	0.016622	0.012430	0.004192	0.290
1.00000	1.00000	0.002609	—		
					mean 0.275

25°C . (Chadwell).

$z-(\text{C}_2\text{H}_5)_2\text{O}$	$z_m-(\text{C}_2\text{H}_5)_2\text{O}$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.008949	—		
0.01360	0.00334	0.009366	0.008846	0.000520	0.156
0.02060	0.00509	0.009597	0.008793	0.000804	0.159
0.03089	0.00769	0.009959	0.008716	0.001243	0.163
0.03485	0.00954	0.010099	0.008662	0.001247	0.152
0.05848	0.01488	0.010883	0.008509	0.002437	0.162
1.00000	1.00000	0.002216	—		
					mean 0.158

Table 4.
 $\text{H}_2\text{O}-\text{C}_6\text{H}_5\text{OH}$ (Howell), 50°C .

$z-\text{C}_6\text{H}_5\text{OH}$	$z_m-\text{C}_6\text{H}_5\text{OH}$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$	$\frac{\delta}{(1-z_m)^2z_m}$
0.00	0.0000	0.005500	—			
0.02	0.0039	0.005696	0.005599	0.000097	0.025	
0.04	0.0079	0.005898	0.005700	0.000198	0.025	
0.06	0.0121	0.006110	0.005807	0.000303	0.025	
0.08	0.0164	0.006340	0.005916	0.000424	0.026	
0.10	0.0208	0.006600	0.006027	0.000573	0.028	
					mean 0.026	
0.70	0.3088	0.01775	0.01366	0.00409		0.040
0.75	0.3650	0.01858	0.01523	0.00335		0.036
0.80	0.4339	0.01981	0.01718	0.00263		0.033
0.85	0.5206	0.02164	0.01970	0.00194		0.034
0.90	0.6328	0.02420	0.02306	0.00141		0.036
0.95	0.7843	0.02820	0.02778	0.00042		(0.053)
						mean 0.036
1.00	1.0000	0.03491	—			

60°C.

$z-C_6H_5OH$	$z_m-C_6H_5OH$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$	$\frac{\delta}{(1-z_m)^3z_m}$
0.00	0.0000	0.004700	—			
0.02	0.0039	0.004850	0.004784	0.000066	0.017	
0.04	0.0079	0.005000	0.004871	0.000129	0.016	
0.06	0.0121	0.005188	0.004962	0.000226	0.019	
0.08	0.0164	0.005360	0.005055	0.000305	0.019	
0.10	0.0208	0.005568	0.005150	0.000418	0.020	
				mean	0.018	
0.70	0.3088	0.01413	0.01137	0.00276		0.027
0.75	0.3650	0.01485	0.01257	0.00228		0.024
0.80	0.4339	0.01591	0.01405	0.00186		0.024
0.85	0.5206	0.01725	0.01591	0.00134		0.023
0.90	0.6328	0.01910	0.01831	0.00079		0.025
0.95	0.7843	0.02180	0.02155	0.00025		(0.032)
					mean	0.025
1.00	1.0000	0.02614	—			

70°C.

$z-C_6H_5OH$	$z_m-C_6H_5OH$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$	$\frac{\delta}{(1-z_m)^3z_m}$
0.00	0.0000	0.004075	—			
0.02	0.0039	—				
0.04	0.0079	—				
0.06	0.0121	—				
0.08	0.0164	—				
0.10	0.0208	0.004771	0.004468	0.000303	0.015	
0.70	0.3088	0.01157	0.00964	0.00183		0.018
0.75	0.3650	0.01215	0.01059	0.00156		0.017
0.80	0.4339	0.01298	0.01174	0.00124		0.020
0.85	0.5206	0.01405	0.01314	0.00091		0.016
0.90	0.6328	0.01547	0.01491	0.00056		0.018
0.95	0.7843	0.01735	0.01720	0.00015		0.019
					mean	0.018
1.00	1.0000	0.02028	—			

As seen from tables 2 and 3, the values $\frac{\delta}{(1-z_m)z_m}$ keep constancy for the studied concentration ranges, and their temperature variations are expressed by the equations:

$$\log \frac{\delta}{(1-z_m)z_m} = 3.513 + \frac{2.00}{1+1} \log (\eta_1 \eta_2)$$

and
$$\log \frac{\delta}{(1-z_m)z_m} = 3.903 + \frac{2.00}{1+1} \log (\eta_1 \eta_2)$$

respectively, whence we may postulate that $\text{CH}_3\text{COOC}_2\text{H}_5 \cdot \text{H}_2\text{O}$ and $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{H}_2\text{O}$ exist in solution.

As to the water and phenol mixture, two hydrates exist in solution. The hydrate $\text{C}_6\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}$ with the stability coefficient $m = 2.00$ at phenol rich solutions is a proof of the extremely low electrical conductivity observed by Howell. The temperature change of the solvation viscosity is completely expressed by the equation:

$$\log \frac{\delta}{(1-z_m)^3 z_m} = 2.680 + \frac{2.00}{3+1} \log (\eta_1^3 \eta_2).$$

The hydrate $\text{C}_6\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ existing at water rich solutions and having

$$\log \frac{\delta}{(1-z_m)z_m} = 1.477 + \frac{1.65}{1+1} \log (\eta_1 \eta_2)$$

indicates from the magnitude of m that it is undoubtedly subjected to the ionic dissociation, $\text{C}_6\text{H}_5\text{OH} \cdot \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{O}' + \text{OH}_3'$, the equilibrium being kept by 2/3 part of undissociated molecule and 1/3 part of dissociated into the two ions.

The present and foregoing studies on the stability coefficient m lead to the conclusion (i) that m takes the value 2 if the molecular compound firmly exists without any dissociation such as the molecular compounds $\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$, $\text{C}_2\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}$, $\text{CH}_3\text{COOC}_2\text{H}_5 \cdot \text{H}_2\text{O}$ and $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{H}_2\text{O}$ —this idea is simply derived from the mathematical consideration of the order of the term, $\eta - \eta_0$, and (ii) that m takes the value less than 2 if the molecular compound suffers ionic dissociation or partial molecular dissociation as are the cases of the monohydrates $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$ ($m = 1.68$) and $\text{C}_6\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ ($m = 1.65$), or is the case of the dihydrate $\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$ ($m = 1.83$) which is in the equilibrium, $\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$.

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EINFACHE VERSUCHE ZUR PRÜFUNG DER ORIENTIERUNG VON MOLEKÜLEN AN DER OBERFLÄCHE DES WASSERS UND DER WÄSSERIGEN LÖSUNGEN.

Von Bun-ichi TAMAMUSHI.

Eingegangen am 6. März, 1934. Ausgegeben am 28. April, 1934.

Eine einfache Methode, die von Frumkin⁽¹⁾ zur Prüfung des Gibbsschen Satzes angegeben worden ist, wird ohne weiteres auch zur Prüfung der Orientierung von Molekülen an der Oberfläche des Wassers angewandt, soweit die Oberflächenschicht monomolekular angenommen werden kann. Löst man also z. B. etwas Laurinsäure in Benzol und bringt die Lösung tropfenweise auf das Wasser, so beobachtet man folgendes: solange die Oberflächenschicht noch nicht gesättigt ist, wird jeder Tropfen in eine flache Scheibe auseinandergezogen, die sich amöbe-artig bewegt und von deren Rändern fortwährend kleine Tröpfchen fortgerissen werden, bis der ganze Tropfen verschwunden ist. Bringt man aber einen Tropfen der Lösung auf eine Oberfläche, die schon gesättigt ist, so verbreitet er sich nicht mehr und das Lösungsmittel verdampft ganz langsam. Misst man die Zeitdauer bis zum Verschwinden des Tropfens mittels einer Stoppuhr, so erkennt man den Übergang ganz scharf.

Auf diese Weise fand ich, dass zur Sättigung einer 243 qcm. grossen Oberfläche des Wassers 0.4 ccm. einer $1 \cdot 10^{-4}\%$ -igen Laurinsäure-lösung notwendig ist. Die Lösung wurde dabei aus einer kalibrierten 1.00 ccm. Pipette tropfenweise auf das Wasser gebracht. Daraus ergibt sich die Sättigungsmenge der Säure zu

(1) *Z. physik. Chem.*, **116** (1925), 498.

$$\frac{4 \cdot 10^{-5}}{243 \cdot 200} = 8.2 \cdot 10^{-10} \text{ Mol/qcm.}$$

Es ergibt sich weiter für das Flächenbedürfnis eines Moleküls der Säure zu

$$\frac{1}{8.2 \cdot 10^{-10} \cdot 6.06 \cdot 10^{23}} = 20 \cdot 10^{-16} \text{ qcm/Molekül.}$$

Ähnliche Versuche habe ich mit Palmitinsäure, Cetylalkohol, Cetylpalmitat und Myrizylpalmitat einmal an der Oberfläche des reinen Wassers und ein anderesmal an der Oberfläche der wässrigen Lösungen (Rohrzucker-, HCl-, KCl-, KBr-, KJ-, LiCl-, NaCl-, MgCl₂-Lösungen) ausgeführt. Die Ergebnisse sind in den folgenden Tabellen zusammengestellt. Die Laurinsäure war das Kahlbaumsche Präparat, die Palmitinsäure das Mercksche, die Cetylalkohol und Cetylpalmitat wurden von Firma Kojima (Tokio) geliefert, und die Myrizylpalmitat wurde in meinem Laboratorium aus Bienenwachs hergestellt. Alle wurden in Benzol gelöst. Die Versuchstemperatur war 15°C.

Die Ergebnisse zeigen, dass bei Laurinsäure, Palmitinsäure und Cetylalkohol die Grösse des Flächenbedarfs des einzelnen Moleküls an der Oberfläche des Wassers mit der bekannten Grösse von Langmuir sowie von Adam übereinstimmt, also entspricht sie einer senkrechten Orientierung des Moleküls an der Oberfläche, während sie bei Cetylpalmitat und Myrizylpalmitat das 2-bis 3-fache von der Grösse eines Kettenkopfes ergibt. Die letzten Ergebnisse führen mich zur Annahme, dass sich die Moleküle von Cetylpalmitat sowie von Myrizylpalmitat an der Oberfläche um ihre polare Gruppe, die vom Wasser stark angezogen wird, biegen und infolgedessen die beiden Ketten nebeneinander parallel und beide senkrecht zur Oberfläche stehen, ohne aber miteinander zusammengedrückt zu sein. Diese Betrachtung über Cetylpalmitat unterscheidet sich von der Langmuirschen.⁽²⁾

In bezug auf die Dehydratationswirkung des gelösten Stoffes auf die polaren Gruppen, ist die Frage der Orientierung von Molekülen an der Oberfläche der wässrigen Lösungen von neuem Interesse.⁽³⁾ Von den oben aufgestellten Ergebnissen sollen einige Tatsachen genannt werden. Der Rohrzucker beeinflusst kaum den Zustand der Oberflächenschicht, was aus seiner geringen Dehydratationswirkung verständlich ist. Die Salzsäure veranlasst in allen Fällen die Schicht sich merklich auszudehnen. Ebenso veranlassen die Salze (KCl, KBr, KJ, KCNS, LiCl, NaCl, MgCl₂) die Schicht sich mehr oder weniger auszudehnen und zwar steigt ihre Wirkung in den folgenden Reihen an:

(2) *J. Amer. Chem. Soc.*, **39** (1917), 1867.

(3) Vgl. Bresler, Chariton, Talmud, u. Talmud, *Z. physik. Chem.*, A. **165** (1933), 195.

Tabelle 1. Laurinsäure

Oberfläche	Sättigungsmenge 10^{-10} Mol/qcm	Flächenbedarf 10^{-16} qcm/Molekül
Wasser	8.2	20
N/2 KCl-Lös.	6.2	27

Tabelle 2. Palmitinsäure

Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 10^{-16} qcm/Molekül	Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 10^{-16} qcm/Molekül
Wasser	8.0	21	N/2 KJ-Lös.	7.2	23
3% Rohrzucker- Lös.	8.0	21	N/2 KCNS-Lös.	8.0	21
N/2 HCl-Lös.	6.4	26	N/2 LiCl-Lös.	7.2	23
N/2 KCl-Lös.	6.4	26	N/2 NaCl-Lös.	8.0	21
N/2 KBr-Lös.	7.2	23	N/2 $MgCl_2$ -Lös.	7.2	23

Tabelle 3. Cetylalkohol

Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 10^{-16} qcm/Molekül	Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 10^{-16} qcm/Molekül
Wasser	7.6	22	N/2 KJ-Lös.	6.8	24
3% Rohrzucker- Lös.	7.6	22	N/2 KCNS-Lös.	7.6	22
N/2 HCl-Lös.	6.2	28	N/2 LiCl-Lös.	7.6	22
N/2 KCl-Lös.	6.2	28	N/2 NaCl-Lös.	7.6	22
N/2 KBr-Lös.	6.8	24	N/2 $MgCl_2$ -Lös.	6.8	24

Tabelle 4. Cetylpalmitat

Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 10^{-16} qcm/Molekül	Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 10^{-16} qcm/Molekül
Wasser	3.4	48	N/2 KJ-Lös.	2.6	64
3% Rohrzucker- Lös.	3.4	48	N/2 KCNS-Lös.	3.0	55
N/2 HCl-Lös.	3.0	55	N/2 LiCl-Lös.	3.2	52
N/2 KCl-Lös.	2.1	77	N/2 NaCl-Lös.	3.4	48
N/2 KBr-Lös.	3.0	55	N/2 $MgCl_2$ -Lös.	3.0	55

Tabelle 5. Myrizylpalmitat

Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 16^{-16} qcm/Molekül	Oberfläche	Sättigungs- menge 10^{-10} Mol/qcm	Flächen- bedarf 10^{-16} qcm/Molekül
Wasser	2.1	77	N/2 KBr-Lös.	1.9	83
3% Rohrzucker- Lös.	2.1	77	N/2 KJ-Lös.	1.9	88
N/2 HCl-Lös.	1.9	88	N/2 LiCl-Lös.	2.1	77
N/2 KCl-Lös.	1.3	123	N/2 NaCl-Lös.	1.9	88
			N/2 MgCl ₂ -Lös	1.9	88

KCNS < KBr, KJ < KCl

NaCl, LiCl < MgCl₂ < KCl

Bei Anionen findet man also auch in diesem Fall die bekannte Lyotrope Reihe, während sich bei Kationen das Kalium-ion merkwürdigerweise abnorm zu verhalten scheint.

Bringt man einen Tropfen auf die Oberfläche der Lösung von solcher Substanz wie KCl und MgCl₂, die auf die Oberflächenschicht stark ausdehnend wirkt, so beobachtet man, dass sich der Tropfen ganz schnell und glatt in eine grosse Scheibe ausbreitet, die sich bald ringartig teilt und von den Rändern reissen sich dann kleine Tröpfchen los. Man beobachtet auch schöne Interferenzfarben, die bei der Ausbreitung des Tropfens auftreten. Sonst verhält sich der Tropfen an der Oberfläche der Lösung solcher Substanz von geringer Dehydratationswirkung, analog wie beim reinen Wasser, aber das Lösungsmittel verdampft etwas schneller.

Von dieser einfachen Methode dürfte man nicht sehr umfangreiche Resultate erwarten. Aber man kann immerhin mittels dieser Methode so schön die Orientierung von Molekülen an der Grenzfläche prüfen und demonstrieren.

Zusammenfassung.

Es wurde eine einfache Methode zur Prüfung der Orientierung von Molekülen an der Oberfläche des Wassers und der wässrigen Lösungen angegeben.

Mittels dieser Methode ergab sich die Grösse eines einzelnen Moleküls an der Oberfläche des Wassers zu $20 \cdot 10^{-16}$ qcm. für Laurinsäure, $21 \cdot 10^{-16}$ qcm. für Palmitinsäure, $22 \cdot 10^{-16}$ qcm. für Cetylalkohol, $48 \cdot 10^{-16}$ qcm. für Cetylpalmitat, und $77 \cdot 10^{-16}$ qcm. für Myrizylpalmitat.

Es wurde mittels dieser Methode die Ausdehnungswirkung von gelösten Stoffen auf die Oberflächenschicht untersucht und wurde gefunden dass die Anionen sich in ihrer Wirkung in der lyotropen Reihe anordnen, während sich bei Kationen das Kalium-ion abnorm verhält.

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HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. VIII.

By Susumu MIYAMOTO.

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Investigations of the reduction of inorganic solid substances by hydrogen in the silent electric discharge were carried out.⁽¹⁾

The apparatus and method of procedure are essentially the same as previously mentioned.⁽¹⁾

Experimental.

(1) **Cupric Nitrate.** Exp. 1. Powdered crystals of cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, employed = 8.00 gr. Time of silent electric discharge = 5 hours. A gas absorption apparatus, which is exactly the same as that employed in the case of calcium nitrate,⁽²⁾ was connected to the discharge tube. Nitrogen peroxide contained in the gaseous reaction products is absorbed by alkaline solution in absorption bottle (1), nitric oxide is then oxidized and absorbed by alkaline solution in absorption bottle (2), and ammonia is absorbed by dilute sulphuric acid in absorption bottle (3).

Water was produced during the reaction and small drops of condensed water were formed on the wall of the discharge tube. A part of the powder in the discharge tube became black and a part reddish brown. A small part of the wall of the discharge tube was covered with a thin film of metallic copper, forming a mirror.

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705.

(2) *Ibid.*, **54** (1933), 89.

Water was added into the discharge tube, well shaken, filtered and washed. A small quantity of insoluble reddish brown powder remained. Most part of the insoluble matter dissolved in hydrochloric acid, producing cupric chloride solution. It is clear that the insoluble substance is principally copper oxide. The filtrate had the following properties.

(1) It was acidic. (2) The solution was placed in a test tube, made alkaline, and heated. The evolution of ammonia was proved. (3) The solution was placed in a test tube, made alkaline, and added to Fehling's solution. On heating, no reduction took place, which proved the absence of hydroxylamine. (4) Sodium hydroxide solution was added to the solution, and the precipitated copper hydroxide was filtered. Potassium iodide solution was added to the filtrate, and the solution was acidified with dilute sulphuric acid, and a few drops of starch solution was added. The solution coloured blue, proving the presence of nitrite.

The alkaline solution in absorption bottle (1) was placed in a test tube and the presence of nitrite was proved. It is therefore certain that nitrogen peroxide is one of gaseous reaction products.

By analyzing the alkaline solution in absorption bottle (2), it was similarly proved that a small quantity of nitric oxide had been produced during the reaction.

The sulphuric acid solution in absorption bottle (3) was placed in a test tube, made alkaline, and heated. The evolution of a small quantity of ammonia was proved.

From these experimental facts it is certain that the principal reaction products are ammonium salt, copper oxide, copper nitrite, nitrogen peroxide nitric oxide, and ammonia.

Exp. 2. The quantity of nitrite produced was determined. The solid reaction products were shaken with water, sodium hydroxide solution sufficient to precipitate the total amount of copper ion was added, and the solid was filtered and washed. The quantity of nitrite contained in the filtrate was determined in the normal manner.

Cupric nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.52 c.c.

Exp. 3. The quantity of ammonium salt produced was determined in the normal manner.⁽³⁾

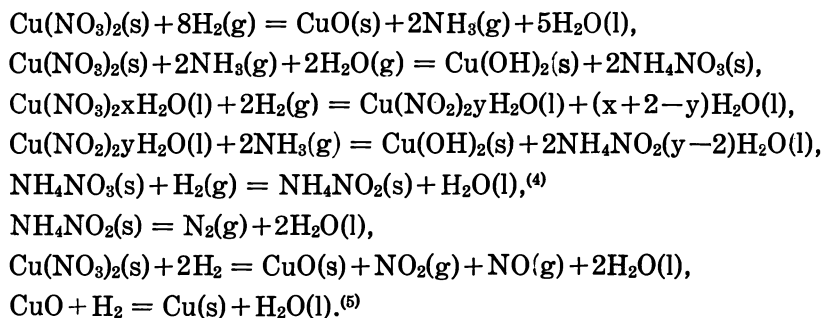
(3) Treadwell, "Kurztes Lehrbuch der analytischen Chemie," 10th ed., Vol. II, p. 483.

Cupric nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 4.54 c.c.

From these experimental facts it seems that the principal reactions in the discharge tube are expressed by the following equations:



(2) **Zirconium Nitrate.** Exp. 1. Zirconium nitrate, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, employed = 7.00 gr. Time of silent electric discharge = 5 hours. A gas absorption apparatus, similar to that employed in the previous case, was connected with the discharge tube. Soon after the electric current was passed, a brown gas, undoubtedly nitrogen peroxide, evolved. Water was produced during the reaction and a part of the powder became moist. Water was added to the discharge tube, well shaken, and filtered. Insoluble white powder is undoubtedly zirconium hydroxide. The filtrate had the following chemical properties.

(1) It was acidic. (2) The absence of hydroxylamine was proved. (3) The presence of nitrite was proved. (4) The presence of ammonium salt was proved.

By analyzing the solutions in absorption bottles (1), (2), and (3), it was proved that nitrogen peroxide and nitric oxide evolved during the reaction, but no ammonia.

From these experimental facts it is certain that the principal reaction products are ammonium salt, zirconium oxide, nitrite, nitrogen peroxide, and nitric oxide.

Exp. 2. The quantity of nitrite produced in the solid reaction products, that of nitrogen peroxide, and that of nitric oxide, were determined.

(4) Miyamoto, *J. Chem. Soc. Japan*, **54** (1933), 715.

(5) *Ibid.*, **53** (1932), 792.

Zirconium nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of potassium permanganate solution of 0.01000 normal equivalent to the quantity of nitrite produced in the discharge tube = 3.26 c.c.

Volume of KMnO_4 -solution of 0.01000 normal, equivalent to the quantity of nitrite produced by the absorption of NO_2 = 153.8 c.c.

Volume of KMnO_4 -solution of 0.01000 normal, equivalent to the quantity of nitrite produced by the absorption of the oxidation product of nitric oxide = 526.6 c.c.

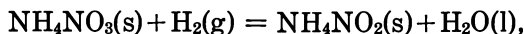
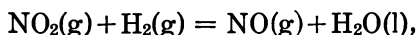
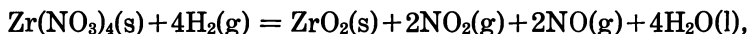
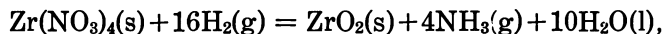
Exp. 3. The quantity of ammonium salt produced was determined.

Zirconium nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 9.45 c.c.

From these experimental facts it seems that the principal reactions are expressed by the following equations:



(3) **Thallos Nitrate.** Exp. 1. The quantity of thallos nitrate, TlNO_3 , employed = 7.00 gr. Time of silent electric discharge = 5 hours. The white powder in the discharge tube became greyish black. Hot water was added to the discharge tube, well shaken, and filtered. A small quantity of insoluble greyish black powder remained. The powder did not dissolve in boiling water. It dissolved in nitric acid or sulphuric acid, forming thallium salt solution. It is therefore certain that the black powder insoluble in boiling water is metallic thallium. The solution, produced by dissolving the solid reaction products in hot water, had the following properties.

(1) It was alkaline, which is undoubtedly due to the presence of thallos hydroxide. (2) It was proved that nearly no ammonium salt was present in the solution. (3) The absence of hydroxylamine was proved. (4) The presence of nitrite was proved.

By analyzing the solutions in absorption bottles (1), (2), and (3), it was proved that nitrogen peroxide and ammonia were gaseous reaction products.

It was thus proved that the principal reaction products are nitrite, thallos hydroxide, metallic thallium, nitrogen peroxide, and ammonia.

Exp. 2. The quantity of nitrite produced was determined. The solid reaction product was dissolved in hot water, thallos ion precipitated by adding acidified sodium chloride solution, and the precipitate was filtered and washed. The quantity of nitrite contained in the filtrate was determined in the normal manner.

Thallos nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of KMnO_4 -solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 31.50 c.c.

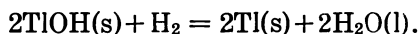
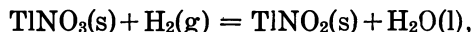
Exp. 3. The quantity of ammonia evolved was determined.

Thallos nitrate employed = 7.00 gr.

Time of silent electric discharge = 4 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed by sulphuric acid solution = 1.13 c.c.

From these experimental facts it seems that the principal reactions are expressed by the following equations:



(4) **Uranyl Nitrate.** Exp. 1. The quantity of uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, employed = 7.00 gr. Time of silent electric discharge = 5 hours. A part of the yellow powder in the discharge tube became reddish brown. Distilled water was added into the discharge tube, well shaken, and filtered. Brown powder remained. It seems that the insoluble substance is principally uranium hydroxide. The filtrate had the following properties.

(1) It was acidic. (2) The solution contained ammonium salt. (3) The solution contained a minute quantity of nitrite. It seems that the nitrite produced is ammonium nitrite. (4) The absence of hydroxylamine was proved. (5) The solution was added to a dilute KMnO_4 -solution and sulphuric acid added. The solution became colourless. As

it was proved that the quantity of nitrite produced is negligible, it is clear that the decolouration is due to the presence of uranous compound, which had been produced during the discharge.

By analyzing the solutions in the absorption bottles (1), (2), and (3), it was proved that neither ammonia nor nitric oxide had been produced during the discharge, but a minute quantity of nitrogen peroxide.

Exp. 2. The quantity of uranous salt produced was determined in the normal manner.⁽⁶⁾

Uranyl nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of KMnO_4 -solution of 0.01000 normal, equivalent to the quantity of uranous salt produced = 10.10 c.c.

As it was proved that nitrite produced is negligible, the value obtained was taken as the quantity of uranous salt.

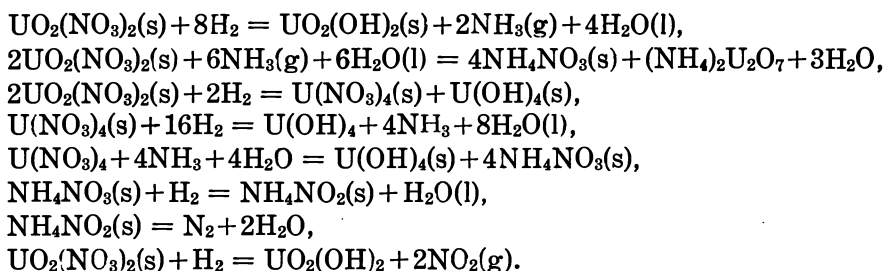
Exp. 3. The quantity of ammonium salt was determined.

Uranyl nitrate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 7.28 c.c.

From these experimental facts it seems that the principal reaction products are ammonium salt, uranous salt, uranium hydroxide, nitrite, and nitrogen peroxide, and that the reactions in the discharge tube are expressed by the following equations:



(5) **Ferric Nitrate.** Exp. 1. The quantity of ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, employed = 8.00 gr. Time of silent electric discharge = 5 hours. A part of the powder gradually became reddish brown, and

(6) Treadwell, "Kurztes Lehrbuch der analytischen Chemie," 10th ed., Vol. II, p. 531.

water was found condensed on the wall of the discharge tube. The solid reaction products were well shaken with water and filtered. Insoluble reddish brown powder was proved to be ferric hydroxide. The filtrate had the following properties.

(1) It was acidic. (2) The solution contained ammonium salt. (3) The solution contained nitrite. (4) The absence of hydroxylamine was proved.

By analyzing the solutions in the absorption bottles (1), (2), and (3), it was proved that nitrogen peroxide and nitric oxide were produced during the discharge, but no ammonia.

It was thus proved that the principal reaction products are ferric hydroxide, ammonium salt, nitrite, nitrogen peroxide, and nitric oxide.

Exp. 2. The quantity of nitrite, that of nitrogen peroxide, and that of nitric oxide produced were determined exactly as in the case of zirconium nitrate.

Ferric nitrate employed = 8.00 gr.

Time of silent electric discharge = 5.5 hours.

Volume of KMnO_4 -solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 15.80 c.c.

Volume of KMnO_4 -solution, equivalent to the quantity of nitrite produced by the absorption of nitrogen peroxide = 235.60 c.c.

Volume of KMnO_4 -solution of 0.01000 normal, equivalent to the quantity of nitrite produced by the absorption of the oxidation product of nitric oxide = 816.30 c.c.

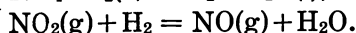
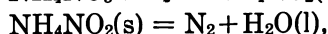
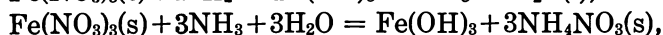
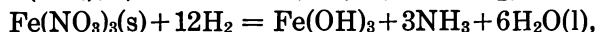
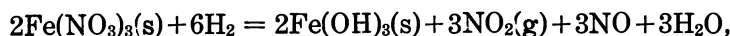
Exp. 3. The quantity of ammonium salt produced was determined.

Ferric nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 1.27 c.c.

From these experimental facts it seems that the principal reactions in the discharge tube are expressed by the following equations:



(6) **Chromic Nitrate.** Exp. 1. The quantity of chromic nitrate, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, employed = 8.00 gr. Time of silent electric discharge

= 5 hours. Water was produced during the reaction and a part of the powder became moist. The solid reaction products were shaken with water and filtered. A small quantity of dark brown powder remained. The insoluble substance was principally chromium hydroxide. The filtrate had the following properties.

(1) It was acidic. (2) The presence of nitrite was proved. (3) The solution contained ammonium salt. (4) The absence of hydroxylamine was proved.

By analyzing the solutions contained in absorption bottles (1), (2), and (3), it was proved that no appreciable amount of nitrogen peroxide, nitric oxide, and ammonia, were produced.

It was thus proved that the principal reaction products are ammonium salt, chromium hydroxide and nitrite.

Exp. 2. The quantity of nitrite was determined.

Chromic nitrate employed = 8.00 gr.

Time of silent electric discharge = 5.5 hours.

Volume of KMnO_4 -solution of 0.01000 normal, equivalent to the quantity of nitrite produced = 1.95 c.c.

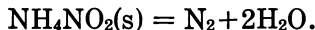
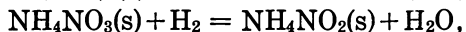
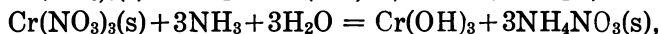
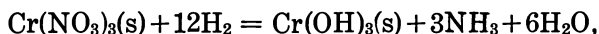
Exp. 3. The quantity of ammonium salt produced was determined.

Chromic nitrate employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

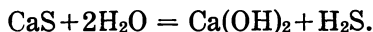
Volume of sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 19.23 c.c.

From these experimental facts it seems that the principal reactions in the discharge tube are expressed by the following equations:



(7) **Calcium Sulphite.** Exp. 1. The quantity of calcium sulphite, $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$, employed = 8.00 gr. Time of silent electric discharge = 5 hours. No appreciable change was observed in the appearance of the white powder in the discharge tube. The solid reaction products were shaken with water. White turbid solution was obtained. It had the following properties.

(1) The solution was alkaline. (2) The solution was placed in a test tube and heated. The evolution of hydrogen sulphide was proved. It is therefore certain that the solution contained sulphide.



The alkaline solution, through which the gas had been passed on leaving the discharge tube, was placed in a test tube, acidified with hydrochloric acid, and heated. Hydrogen sulphide evolved.

It was thus proved that calcium sulphide, calcium hydroxide, and hydrogen sulphide are the principal reaction products.

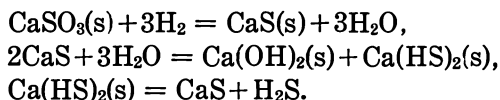
Exp. 2. On leaving the discharge tube the gas was passed through two absorption bottles, containing alkali solutions, and the quantity of hydrogen sulphide absorbed was determined in the normal manner.

Calcium sulphite employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.20 c.c.

From these experimental facts it is concluded that the principal reactions in the discharge tube are expressed by the following equations:



(8) **Sodium Sulphite.** Exp. 1. The quantity of anhydrous sodium sulphite, Na_2SO_3 , employed = 8.00 gr. Time of silent electric discharge = 5 hours. No appreciable change was observed in the appearance of the powder in the discharge tube. The solid reaction products were dissolved in water. Light brown solution obtained had the following properties.

(1) It was alkaline. (2) The solution was placed in a test tube, sodium hydroxide solution and a few drops of sodium nitroprusside solution added. The solution coloured orange, proving the absence of sulphide.

The alkaline solution, through which the gas had been passed on leaving the discharge tube, was placed in a test tube, acidified, and heated. The evolution of hydrogen sulphide was proved.

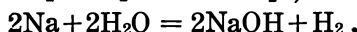
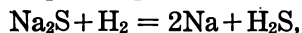
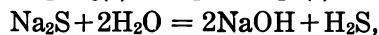
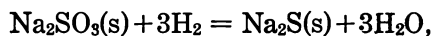
Exp. 2. The quantity of hydrogen sulphide was determined exactly as in the case of calcium sulphite.

Sodium sulphite employed = 8.00 gr.

Time of silent electric discharge = 6 hours.

Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of H_2S produced = 0.99 c.c.

From these experimental facts it is concluded that the principal reactions in the discharge tube are expressed by the following equations:



Further experiment will be necessary to decide the occurrence of the third reaction.

Summary.

The chemical reactions in the silent electric discharge were studied when hydrogen reacted on the following inorganic solid substances.

(1) Cupric nitrate. Reaction products:—ammonium salt, copper oxide, metallic copper, nitrite, nitrogen peroxide, nitric oxide, and ammonia.

(2) Zirconium nitrate. Reaction products:—ammonium salt, zirconium oxide, nitrite, nitrogen peroxide, and nitric oxide.

(3) Thallous nitrate. Reaction products:—Nitrite, thallous hydroxide, metallic thallium, nitrogen peroxide, and ammonia gas.

(4) Uranyl nitrate. Reaction products:—ammonium salt, uranous salt, uranium hydroxide, nitrite, and nitrogen peroxide.

(5) Ferric nitrate. Reaction products:—ammonium salt, ferric hydroxide, nitrite, nitrogen peroxide, and nitric oxide.

(6) Chromic nitrate. Reaction products:—ammonium salt, chromium hydroxide, and nitrite.

(7) Calcium sulphite. Reaction products:—Calcium sulphide, calcium hydroxide, and hydrogen sulphide.

(8) Sodium sulphite. Reaction products:—Sodium hydroxide, and hydrogen sulphide.

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HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. IX.

By Susumu MIYAMOTO.

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Investigations of the reduction of a number of inorganic solid substances by hydrogen in the silent electric discharge have been carried out over a considerable period: there follows an account of the results obtained since the publication of the previous papers.⁽¹⁾ The apparatus and method of procedure are essentially the same as previously mentioned.⁽¹⁾

Experimental.

(1) **Potassium Sulphite.** Exp. 1. A qualitative experiment was first carried out, 8.00 gr. of anhydrous potassium sulphite being employed. The result was exactly the same as in the case of sodium sulphite.⁽²⁾ The evolution of hydrogen sulphide was proved.

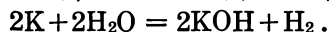
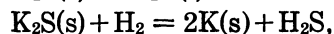
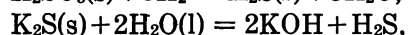
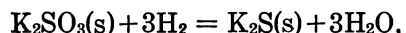
Exp. 2. The quantity of hydrogen sulphide produced was determined in the normal manner.

Potassium sulphite employed = 8.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.55 c.c.

From these experimental facts it is concluded that the principal reactions in the discharge tube are expressed by the following equations:



(2) **Cadmium Bromide.** Exp. 1. Seven grams of the powdered crystals of cadmium bromide, $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, were employed. On leaving

(1) Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223.

(2) Miyamoto, *ibid.*, **54** (1933), 1231.

discharge tube, the gas was passed through a small absorption bottle, containing about 5 c.c. of distilled water. The absorption bottle employed is shown by Fig. 1. The white powder in the discharge tube gradually became black and small drops of water were found condensed on the wall of the discharge tube. After the lapse of 6 hours the electric current was stopped. The water drops formed on the wall of the discharge tube were proved to be acidic. The solid re-

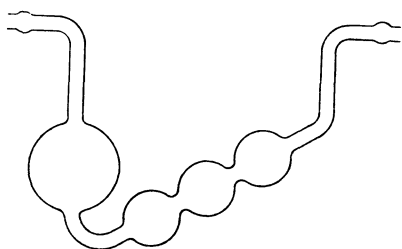


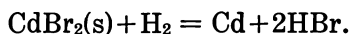
Fig. 1.

action products were shaken with water and filtered. A small quantity of greyish black powder remained. The filtrate was acidic, which was undoubtedly due to the presence of hydrogen bromide. On rubbing with a glass rod, the greyish black powder showed metallic lustre, and it dissolved in hydrochloric acid with the evolution of fine gas bubbles.

The solution produced was proved to contain cadmium chloride. It is therefore certain that the insoluble greyish black powder is metallic cadmium.

The water in the absorption bottle was weakly acidic, and on adding silver nitrate solution, a small quantity of silver bromide precipitated.

From these experimental results it is concluded that the principal reaction in the discharge tube is



(3) **Potassium Perchlorate.** Exp. 1. The quantity of potassium perchlorate, KClO_4 , employed = 8.00 gr. Time of silent electric discharge = 5 hours. No appreciable change was observed in the appearance of the powder in the discharge tube. The solid reaction product was shaken with water and filtered. On adding silver nitrate solution to the filtrate, white precipitate was produced, proving the presence of chloride.

Exp. 2. The quantity of chloride produced was determined by Volhard's method.⁽³⁾

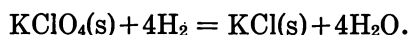
Potassium perchlorate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of potassium chloride produced = 20.10 c.c.

(3) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 10th ed., Vol. II, p. 614.

From these facts it is concluded that the principal reaction in the discharge tube is expressed by



(4) **Mercuric Cyanide.** Exp. 1. The quantity of mercuric cyanide, $\text{Hg}(\text{CN})_2$, employed = 7.00 gr. Time of silent electric discharge = 7 hours. On leaving the discharge tube, the gas was passed through a gas absorption bottle, containing about 5 c.c. of potassium hydroxide solution. The powder in the discharge tube became slightly grey. The solid reaction product was shaken with water. Fine drops of metallic mercury were found on the bottom of the container.

The alkaline solution in the absorption bottle was placed in a test tube, heated with a few drops of ferrous sulphate solution, and acidified. The solution coloured blue, and, on standing, a small quantity of Prussian blue precipitated, proving the presence of cyanide.⁽⁴⁾

It was thus proved that the principal reaction products are metallic mercury and hydrogen cyanide.

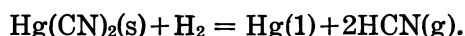
Exp. 2. Two absorption bottles, containing potassium hydroxide solutions were connected with the discharge tube, and the quantity of hydrogen cyanide absorbed was determined by Liebig's method.⁽⁵⁾

Mercuric cyanide employed = 7.00 gr.

Time of silent electric discharge = 7 hours.

The quantity of hydrogen cyanide produced = 0.00452 gr.

From these experimental results it is concluded that the principal reaction in the discharge tube is expressed by



(5) **Mercuric Thiocyanate.** Exp. 1. The quantity of mercuric thiocyanate, $\text{Hg}(\text{SCN})_2$, employed = 7.00 gr. Time of silent electric discharge = 5 hours. On leaving the discharge tube the gas was passed first through distilled water and then through potassium hydroxide solution. The white powder in the discharge tube gradually became yellowish red and after the lapse of a few hours the powder became black. A part of the wall of the discharge tube was covered with a thin film of metallic mercury, forming a mirror. The reaction product in the discharge tube was shaken with water and filtered. The filtrate was

(4) Treadwell, "Kurztes Lehrbuch der analytischen Chemie," 13th ed., Vol. I, p. 306.

(5) Ibid., 10th ed., Vol. II, p. 617.

acidic. The insoluble substance was well washed with water, placed in a test tube, and heated with hydrochloric acid of about 8 normal. The evolution of hydrogen sulphide was proved.

The liquid in the first absorption bottle was examined. It had the following properties.

(1) It was acidic. (2) The solution was placed in a test tube, and a small quantity of ferric chloric solution was added. The solution became red, proving the presence of thiocyanic acid. (3) The presence of hydrocyanide was proved exactly as in the case of mercuric cyanide.

The alkaline solution in the second absorption bottle had the following properties.

(1) The presence of cyanide was proved. (2) The presence of sulphide was proved.

From these facts it is certain that the principal reaction products are metallic mercury, mercuric sulphide, hydrogen cyanide, hydrogen sulphide, and thiocyanic acid.

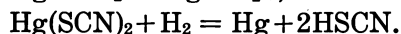
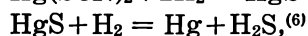
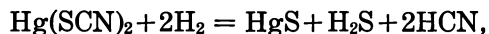
Exp. 2. The quantity of hydrogen sulphide evolved was determined.

Mercuric thiocyanate employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 7.60 c.c.

From these facts it seems that the principal reactions in the discharge tube are expressed by the following equations:



(6) **Silver Cyanide.** Exp. 1. The quantity of silver cyanide, AgCN, employed = 7.00 gr. Time of silent electric discharge = 5 hours. On leaving the discharge tube, the gas was passed through an absorption bottle, containing about 5 c.c. of potassium hydroxide solution. The white powder in the discharge tube gradually became black. A part of the black powder in the discharge tube had metallic lustre, showing the formation of metallic silver. It was proved exactly as in the case of mercuric cyanide that hydrogen cyanide was one of the reaction products.

Exp. 2. The quantity of hydrogen cyanide produced was determined exactly as in the case of mercuric cyanide.

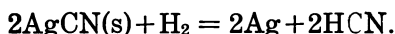
(6) Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 794.

Silver cyanide employed = 7.00 gr.

Time of silent electric discharge = 5 hours.

The quantity of hydrogen cyanide produced = 0.00138 gr.

It is concluded that the reaction in the discharge tube is expressed by



(7) **Sodium Thiocyanate.** Exp. 1. The quantity of sodium thiocyanate, NaSCN, employed = 7.00 gr. Time of silent electric discharge = 7 hours. As sodium thiocyanate is a very hygroscopic substance, the quantity of water included in the reacting substance was considerable. The powder in the discharge tube gradually coloured light yellow and a part became moist. The formation of hydrogen cyanide and hydrogen sulphide was proved exactly as in the case of mercuric thiocyanate.

The solid reaction product was dissolved in water. Light yellow solution was produced. The solution was alkaline. The solution was placed in a test tube, and a small quantity of sodium hydroxide solution and a few drops of sodium nitroprusside solution were added. The solution coloured reddish violet, proving the presence of sulphide.⁽⁷⁾

It was thus proved that the principal reaction products are sodium sulphide, hydrogen cyanide, and hydrogen sulphide.

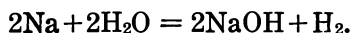
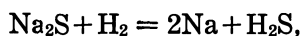
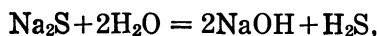
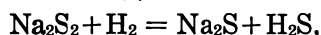
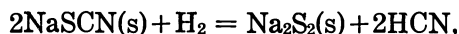
Exp. 2. The quantity of hydrogen sulphide produced was determined.

Sodium thiocyanate employed = 7.00 gr.

Time of silent electric discharge = 6 hours.

Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.10 c.c.

From these experimental facts it seems that the principal reactions in the discharge tube are expressed by the following equations:



(8) **Lead Thiocyanate.** Exp. 1. The quantity of lead thiocyanate, Pb(SCN)_2 , employed = 7.00 gr. Time of silent electric discharge = 6

(7) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 13th ed., Vol. I, p. 391.

hours. The evolution of hydrogen cyanide and hydrogen sulphide was proved exactly as in the case of mercuric thiocyanate. The powder in the discharge tube gradually became black. The solid reaction product was shaken with water, filtered, and washed. The filtrate was acidic. The insoluble substance was placed in a test tube, and heated with hydrochloric acid. The evolution of hydrogen sulphide was proved.

It was thus proved that the principal reaction products are lead sulphide, hydrogen cyanide, and hydrogen sulphide.

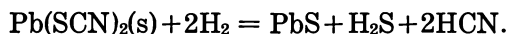
Exp. 2. The quantity of hydrogen sulphide evolved was determined.

Lead thiocyanate employed = 7.00 gr.

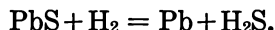
Time of silent electric discharge = 6 hours.

Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.20 c.c.

From these experimental facts it is concluded that the principal reaction in the discharge tube is expressed by



As it was proved that lead sulphide is reduced further,⁽⁸⁾ the following reaction must have occurred in the discharge tube:



(9) **Potassium Cyanide.** The quantity of potassium cyanide, KCN, employed = 7.00 gr. Time of silent electric discharge = 7 hours. The alkaline solution, through which the gas had been passed on leaving the discharge tube, was analyzed. No cyanide was detected. The powder in the discharge tube was analyzed. No appreciable change was observed.

It was thus proved that potassium cyanide was hardly reduced under the conditions of this experiment.

Summary.

The chemical reactions in the silent electric discharge were studied when hydrogen reacted on the following inorganic solid substances.

(1) Potassium sulphite. Reaction products:—hydrogen sulphide and potassium hydroxide.

(2) Cadmium bromide. Reaction products:—metallic cadmium and hydrogen bromide.

(8) Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 795.

(3) Potassium perchlorate. Reaction products:—potassium chloride and water.

(4) Mercuric cyanide. Reaction products:—metallic mercury and hydrogen cyanide.

(5) Mercuric thiocyanate. Reaction products:—mercuric sulphide, metallic mercury, hydrogen cyanide, hydrogen sulphide, and thiocyanic acid.

(6) Silver cyanide. Reaction products:—metallic silver and hydrogen cyanide.

(7) Sodium thiocyanate. Reaction products:—sodium sulphide, hydrogen sulphide, and hydrogen cyanide.

(8) Lead thiocyanate. Reaction products:—lead sulphide, hydrogen sulphide, and hydrogen cyanide.

(9) Potassium cyanide. It was proved that potassium cyanide was hardly reduced under the conditions of this experiment.

The writer wishes to express his appreciation of a grant from the Imperial Academy towards the expenses of this research.

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**SUR LA FORMATION DE COMPOSÉS MOLÉCULAIRES
ENTRE LES CHALCONES ET LES CORPS
NITROAROMATIQUES.**

Par Tei-ichi ASAHINA.

Reçu le 10 mars 1934. Publié le 28 avril 1934.

Dans notre rapport précédent, nous avons indiqué l'existence de composés moléculaires formés aux dépens de divers dérivés de chalcones et d'acide picrique. Nous avons, en même temps, discuté la raison de leur formation.⁽¹⁾ Il est très probable que le groupement nitro des composés

(1) Ce bulletin, **9** (1934), 131.

nitroaromatiques y joue un rôle important. Pour vérifier cette hypothèse, nous avons examiné s'il y a formation de composés moléculaires entre quelques chalcones et divers composés nitroaromatiques, et nous avons constaté qu'il y en a beaucoup. Nous avons d'abord recherché s'il est possible d'obtenir des composés moléculaires entre ces chalcones et quelques corps mononitroaromatiques. Les résultats de ces investigations sont donnés ci-dessous. Nous avons ensuite étudiés les corps aromatiques polynitrés. Nous en donnerons le compte-rendu dans notre prochain rapport.

Partie expérimentale.

I. Étude du système : *o*-Nitrotoluène et 3, 4-méthylènedioxybenzal-acétophénone.

La chalcone a été préparé de la façon décrite dans notre rapport précédent⁽¹⁾⁽²⁾ (point de fusion 121°) et nous avons utilisé le nitrotoluène commercial après recristallisation dans l'alcool (p.d. f. 53°).

Table 1. (Voyez la Fig. 1)

Pourcentages		Points de dégel °C	Points de congel °C
de chalcone	de nitro- toluène		
0,0	100,0	—	53,0
5,0	95,0	45,2	50,8
12,5	87,5	45,7	48,0
19,0	81,0	45,8	47,5
21,9	78,1	45,7	53,0
30,0	70,0	45,5	65,0
40,0	60,0	45,5	75,0
55,3	44,7	45,8	91,0
67,0	33,0	46,0	103,0
78,4	21,6	46,0	109,3
90,0	10,0	49,0	117,0
92,2	7,8	56,0	119,0
100,0	0,0	—	121,0

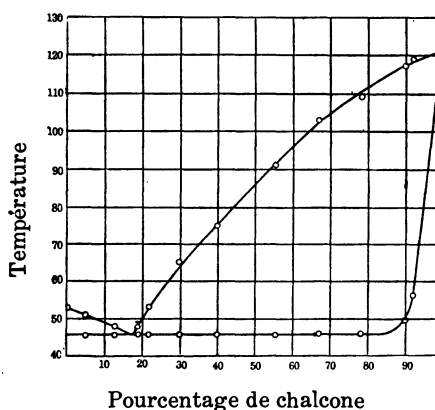


Fig. 1.

(2) St. v. Kostanecki et M. Schneider, *Ber.*, **29** (1896), 1892.

Il n'y a qu'un point eutectique (45,5°, chalcone 17,5%) et on sait qu'il n'y a pas de formation de composé moléculaire.

II. Étude du système : *o*-Nitrophénol et benzal-acétophénone.

Table 2. (Voyez la Fig. 2)

Pourcentages		Points de dégel °C	Points de congel °C
de chalcone	de nitro-phénol		
0,0	100,0	—	45,0
8,46	91,54	23,0	42,3
25,5	74,5	22,3	35,5
38,0	62,0	22,0	29,5
40,4	59,6	22,0	29,0
48,0	52,0	22,0	24,5
53,4	46,6	22,5	29,5
66,2	33,8	22,7	37,0
77,5	22,5	23,0	44,0
82,7	17,3	23,2	48,0
91,1	8,9	24,0	53,0
96,4	3,6	31,0	56,7
100,0	0,0	—	57,8

Le nitrophénol utilisé a été obtenu par recristallisation du produit commercial dans l'alcool (p. d. f. 45,0°) et la chalcone a été obtenue par condensation d'acétophénone avec benzaldehyde (p. d. f. 57,8°).⁽³⁾

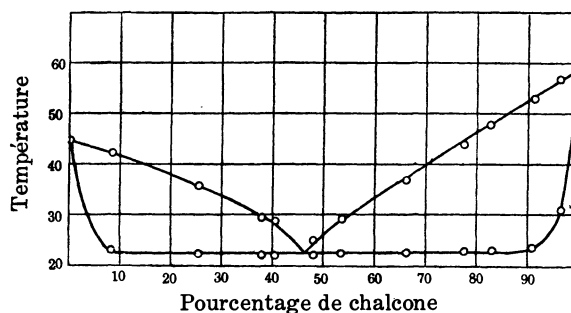


Fig. 2.

Il n'y a qu'un point eutectique (22,5°, chalcone 46%) de telle sorte qu'il n'existe aucun composé moléculaire.

III. Étude du système : *o*-Nitrophénol et 3,4-méthylènedioxybenzal-acétophénone.

Table 3. (Voyez la Fig. 3)

Pourcentages		Points de dégel °C	Points de congel °C
de chalcone	de nitro-phénol		
0,0	100,0	—	45,0
7,0	93,0	39,3	44,0
16,0	84,0	39,2	41,0
20,0	80,0	39,2	45,5
27,5	72,5	39,3	55,5
46,5	53,5	39,2	80,0
54,5	45,5	39,3	88,5
70,5	29,5	39,5	105,5
86,0	14,0	39,7	114,5
100,0	0,0	—	121,0

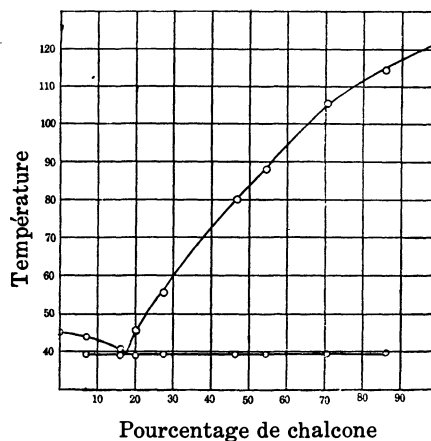


Fig. 3.

(3) St. v. Kostanecki et G. Rossbach, *Ber.*, **29** (1896), 1492.

Dans ce cas, de même que les deux cas précédents, il n'y a qu'un point eutectique (39°, chalcone 18%) et on ne constate pas de formation de composé moléculaire.

Table 4. (Voyez la Fig. 4)

Pourcentages		Points de dégel °C	Points de congel °C
de chal- cone	de nitro- phénol		
0,0	100,0	—	96,0
7,8	92,2	62,5	93,7
16,0	84,0	61,5	90,6
23,3	76,7	62,0	87,0
32,0	68,0	62,0	80,2
43,5	56,5	61,8	70,0
47,0	53,0	61,5	64,8
49,3	50,7	62,0	64,0
51,0	49,0	62,0	63,5
52,0	48,0	62,0	64,2
55,0	45,0	62,0	65,5
60,5	39,5	53,0	65,3
67,8	32,1	45,5	64,6
75,3	24,7	45,0	61,2
80,2	19,8	45,4	55,0
87,2	12,8	45,0	49,0
90,1	9,9	45,0	50,0
93,5	6,5	45,5	54,0
100,0	0,0	0,0	57,8

Table 5. (Voyez la Fig. 5)

Pourcentages		Points de dégel °C	Points de congel °C
de chal- cone	de nitro- phénol		
0,0	100,0	—	96,0
5,0	95,0	79,0	94,8
13,8	86,2	77,5	91,5
21,7	78,3	77,7	87,0
33,1	66,9	77,2	81,0
39,5	60,5	77,2	86,0
48,6	51,4	77,5	91,5
55,0	45,0	79,2	94,0
60,0	40,0	85,0	95,8
63,0	37,0	91,3	96,1
65,4	34,6	92,3	95,0
68,1	31,9	91,5	95,2
70,0	30,0	91,0	94,1
73,0	27,0	91,5	94,2
74,3	25,7	91,2	95,2
78,8	21,2	91,5	102,0
86,6	13,4	91,8	111,5
93,1	6,9	92,0	117,2
100,0	0,0	—	121,0

IV. Étude du système : *m*-Nitrophénol et benzal-acétophénone.

On a utilisé le nitrophénol commercial après recristallisation dans l'alcool (p. d. f. 96,0°).

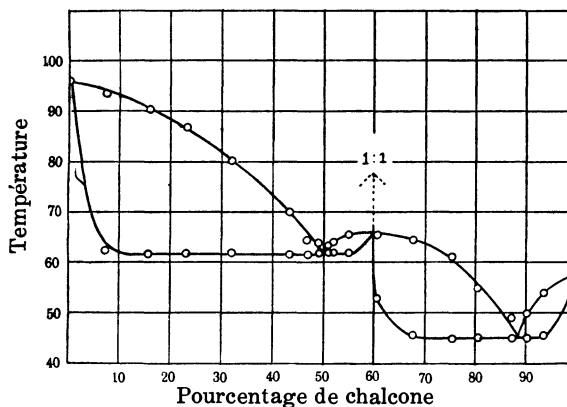


Fig. 4.

Dans ce système il y a deux points eutectiques (62°, chalcone 50% et 45°, chalcone 88,5%) et un point distectique (65°, chalcone 59,9% c'est-à-dire du rapport moléculaire d'un pour un). On sait ainsi qu'il y a formation d'un composé moléculaire de formule $\text{NO}_2\text{C}_6\text{H}_4\text{OH} \cdot \text{C}_6\text{H}_5\text{COCH} = \text{CHC}_6\text{H}_5$.

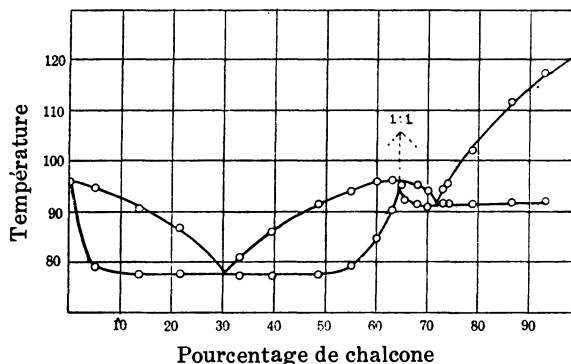


Fig. 5.

V. Étude du système : *m*-Nitrophénol et 3, 4-méthylènedioxybenzal-acétophénone.

Il y a deux points eutectiques (77,5°, chalcone 30,5% et 91,5°, chalcone 72%) et un point distectique (96,5°, chalcone 64,4% c'est-à-dire du rapport moléculaire de 1:1), de telle sorte qu'il y a formation d'un composé moléculaire de formule $\text{NO}_2\text{C}_6\text{H}_4\text{OH} \cdot \text{C}_6\text{H}_5\text{COCH} = \text{CHC}_6\text{H}_3\text{O}_2\text{CH}_2$.

Table 6. (Voyez la Fig. 6)

Pourcentages		Points de dégel °C	Points de congel °C
de chalcone	de nitro-phénol		
0,0	100,0	—	113,0
9,9	90,1	80,0	108,0
15,4	84,6	78,0	104,7
20,0	80,0	78,0	104,0
28,0	72,0	78,0	97,0
36,3	63,7	78,0	90,0
43,5	56,5	78,0	82,3
51,5	48,5	78,0	85,0
57,9	42,1	79,5	86,3
61,4	38,6	76,5	86,8
63,0	37,0	74,0	86,5
68,0	32,0	51,0	85,0
73,0	27,0	51,0	82,0
83,0	17,0	51,0	73,0
91,0	9,0	51,0	56,0
96,0	4,0	51,3	55,0
100,0	0,0	—	57,8

VI. Étude du système : *m*-Nitrophénol et benzal-acétophénone.

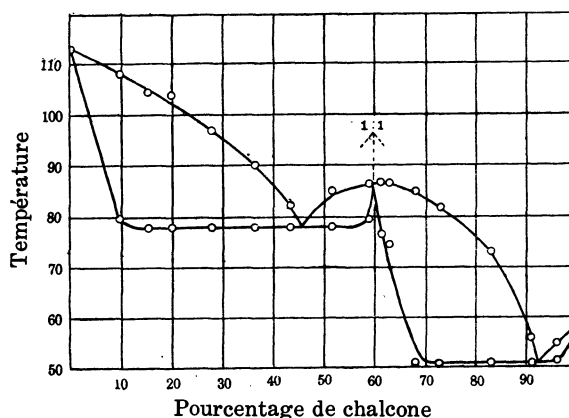


Fig. 6.

Table 7. (Voyez la Fig. 7)

Pourcentages		Points de dégel °C	Points de congel °C
de chalcone	de nitro-phénol		
0,0	100,0	—	113,0
5,0	95,0	91,8	111,5
9,5	90,5	91,6	110,0
20,0	80,0	91,5	104,0
27,5	72,5	91,6	98,0
34,5	65,5	91,5	95,0
47,7	52,3	91,3	104,5
57,0	43,0	91,5	108,5
60,0	40,0	92,5	109,0
63,0	37,0	106,0	109,0
66,4	33,6	102,0	109,0
69,0	31,0	100,5	108,2
73,5	26,5	100,0	107,0
80,4	19,6	100,3	104,0
86,0	14,0	100,0	111,0
92,0	8,0	100,5	116,2
96,0	4,0	102,5	119,0
100,0	0,0	0,0	121,0

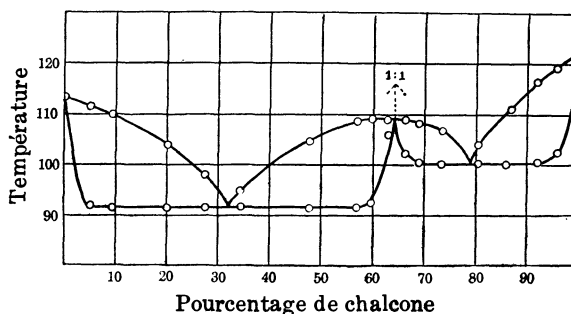


Fig. 7.

VII. Étude du système : *p*-Nitrophénol et 3,4-méthylènedioxy-benzal-acétophénone.

Dans ce cas aussi, il y a deux points eutectiques (91,7°, chalcone 32% et 100°, chalcone 79,0%) et un point distectique 109,0°, chalcone 64,4% c'est-à-dire du rapport moléculaire de 1 : 1) et on sait ainsi qu'il y a formation d'un composé moléculaire de formule $\text{NO}_2\text{C}_6\text{H}_4\text{OH} \cdot \text{C}_6\text{H}_5\text{COCH} = \text{CHC}_6\text{H}_3\text{O}_2\text{CH}_2$. En résumé on constate que les chalcones peuvent former avec les corps nitroaromatiques des composés moléculaires. Leur non-production aux dépens du *o*-nitrophénol et du *p*-nitrotoluène sera discutée lorsque de nouvelles expériences nous auront fourni une base suffisante d'appréciation.

En terminant nous avons l'agréable devoir d'exprimer nos vifs remerciements à M. K. Yokoyama, aide privé, qui nous a aidé dans nos expériences et aussi à M. le prof. Y. Shibata qui nous a donné les plus utiles conseils.

Le Dr. Motte de la Maison franco-japonaise de Tokio, a eu la bonté de revoir ce mémoire au point de vue linguistique : nous l'en remercions sincèrement ici.

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**FUNGI (*Trichophyton interdigitale*, *Trichophyton violaceum*, *Epidermophyton inguinale*, and *Aspergillus oryzae*)
AND FUNGICIDES.**

By Taichi HARADA.

Received February 19th, 1934. Published April 28th, 1934.

Introduction.

Reports on the isolations of fungi such as *Trichophyton interdigitale*, *Trichophyton violaceum*, *Epidermophyton inguinale*, *Aspergillus*, and other fungi from infected nails, feet, skin lesions and even from the sweat of

normal person have been made by various investigators.⁽¹⁾ Studies concerned with their reactions to chemotherapy, and with *Aspergillus oryzae* in relation to food have been made. Certain substances such as mercurial compounds,⁽²⁾ thallium acetate,⁽³⁾ an ointment containing salicylic or benzoic acid⁽⁴⁾ or both,⁽⁵⁾ volatile oils,⁽⁶⁾ various dyes⁽²⁾⁽⁷⁾⁽⁸⁾, etc. have been found effective to prevent the growth or to kill the fungi at certain concentrations and under given conditions. However the concentrations required are beyond both the toleration of the human palate and the safety line for use either on the body or for preservation of food. Therefore it seemed important to study at first hand the influence both of the pH of the culture medium and of the concentration of the chemicals in relation to the worth of the various fungicides.

Experimental.

Description of Fungi. *Trichophyton interdigitale* (Kaufmann-Wolf) was found to be a fluffy white colony which grew rapidly in a rounded mass, and then spread over the medium. The colony later became cream-coloured, powdery and areolar.

Epidermophyton inguinale was greenish buff in colour, had a pyramidal form of *Ascia* and gradually covered the entire surface of the medium. No conidia were formed, but it was easily identified by fuseaux which were found on aerial hyphae.

(1) E. M. Rockwood, *Arch. Dermat. and Syph.*, **22** (1930), 395; F. D. Weidman, *ibid.*, **2** (1920), 703; **13** (1926), 374; S. O. Chambers and F. D. Weidman, *ibid.*, **18** (1928), 568; A. Castellani, *ibid.*, **17** (1928), 194, 354; J. F. Burgees, *ibid.*, **14** (1926), 851; O. S. Ormsby and J. H. Mitchell, *J.A.M.A.*, **67** (1916), 711; F. W. Tanner and B. Feuer, *Arch. Dermat. and Syph.*, **1** (1920), 365; M. B. Hartzell, *ibid.*, **1** (1920), 1; M. M. Keston, B. K. Ashford, R. W. Benham, C. W. Emmons, and M. C. Moss, *ibid.*, **25** (1932), 1046; A. Strickler, E. A. Ozeller and R. P. Zaletel, *ibid.*, **25** (1932), 1028; R. C. Jamieson and A. McCrea, *ibid.*, **25** (1932), 321; C. W. Emmons, *ibid.*, **25** (1932), 987; G. M. Mackee and G. M. Lewis, *ibid.*, **23** (1931), 445; H. Fox and R. W. Fowlkes, *ibid.*, **11** (1925), 446; H. Fox, *ibid.*, **13** (1926), 398; M. F. Engman, *ibid.*, **13** (1926), 352; M. B. Sulzberger, *ibid.*, **18** (1928), 891; H. Odlan and R. E. Hoffstadt, *ibid.*, **20** (1929), 335; A. G. Goud and E. K. Carter, *ibid.*, **22** (1930), 225; S. M. Peck and G. Salomon, *ibid.*, **24** (1931), 554; B. Bleck, *Brit. J. Dermat.*, **42** (1930), 549; O. L. Levin and S. H. Silvers, *Arch. Dermat. and Syph.*, **23** (1931), 1094.

(2) J. F. Schamberg and Kolmer, *Arch. Dermat. and Syph.*, **6** (1922), 746.

(3) B. E. Felden, *ibid.*, **17** (1928), 182.

(4) J. H. Stokes, *J. Am. M. A.*, **98** (1932), 1127.

(5) J. H. Mitchell, *Arch. Dermat. and Syph.*, **5** (1922), 174.

(6) H. B. Myer and C. H. Thirnes, *J. Am. M. A.*, **84** (1925), 1985.

(7) D. L. Farley, *Arch. Dermat. and Syph.*, **2** (1920), 459.

(8) L. H. Leonian, *ibid.*, **25** (1932), 1016.

Trichophyton violaceum developed (within four days) with a glistening surface. Within nine days a black violet colour developed from the center of the colony. No conidia were formed.

Aspergillus oryzae grew in a fluffy rounded white colony, rapidly spread over the medium, and gradually became dark yellowish green. Finally it became powdery and brownish green. It had characteristic conidiophores which made its identification easy.

Culture Medium. A specific group of fungi has a specific preference for a culture medium and produces a colony of definite shape and colour. For the present experiment Sabouroud's culture medium was prepared from the following ingredients:

Distilled water	Agar-agar	Peptone	Dextrose	Glycerine	Sodium chloride
1000 c.c.	15 gr.	15 gr.	20 gr.	5 c.c.	5 gr.

The mixture was boiled gently for one and a half hours until it became clear. The solution was then made up to the original weight with water and filtered through absorbent cotton. It was found, by potentiometric method using quinhydrone and calomel electrodes, to have a *pH* of about 5.4 which is similar to that of normal skin surface.⁽⁹⁾ However the *pH* values of both sweat and blood of a normal person were found to be 7.33 which is also the optimum *pH* of pathogenic fungi. The *pH* of this medium was therefore adjusted approximately to 7.3 by means of about 5 c.c. of normal sodium hydroxide. Seven cubic centimeter portions of this solution, in test tubes of 20 c.c. capacity, plugged with absorbent cotton, were sterilized in an autoclave under 15 pounds pressure for 30 minutes. This treatment lowered the *pH* of the medium to 6.9 (± 2). Nevertheless it gave rich growth. The tubes were stored in an ice-box to prevent evaporation of moisture.

The various fungicide solutions were made up in concentrations varying from 0.3 to 100 per cent. depending upon their effectiveness as fungicides.

For each fungicide four series, each consisting of (usually) seven tubes of the medium, were taken. These were melted in a hot water bath, and then cooled to about 40°C. With a sterile 1 c.c. graduated pipette, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 c.c. of a fungicide solution were carefully added to the respective series. These were well mixed and the surface of each of the four series of media was then inoculated with a different fungus by means of a sterile platinum wire.

(9) O. L. Levin and S. H. Silvers, *Arch. Dermat. and Syph.*, **25** (1932), 823.

Microphotographs of Fungi

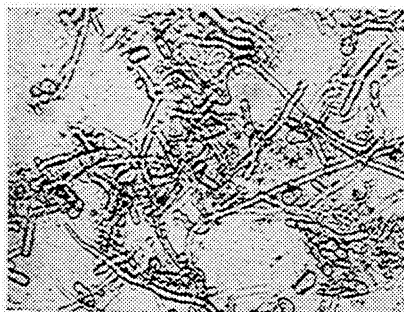
*Trichophyton interdigitale* × 450

Fig. 1.

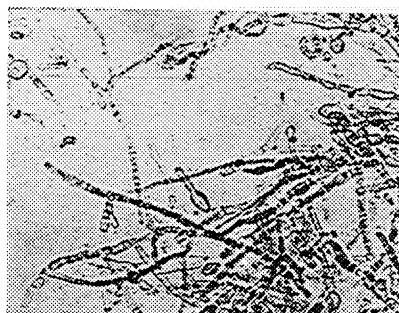
*Trichophyton violaceum* × 450

Fig. 2.

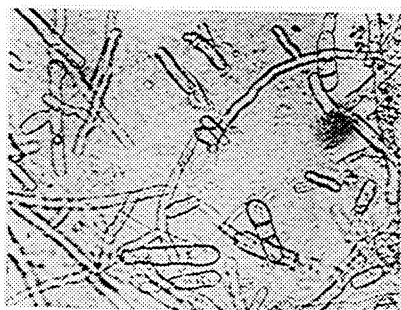
*Epidermophyton inguinale* × 450

Fig. 3.

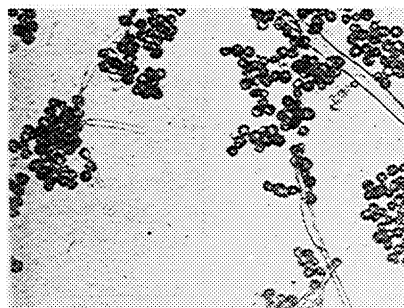
*Aspergillus oryzae* × 450

Fig. 4.

The tubes were kept at room temperature for more than three months of the period from April to September (of 1932 and 1933) which is the most favourable season for the growth of most of fungi. They were examined from time to time and the observations recorded. The results are tabulated giving the ratios of the chemicals to the amounts of medium. The figures at the left indicate the concentration at which the fungi grew while the figures at the right indicate the concentration too high for growth. However these values represent approximations only.

Discussion.

Solutions such as those of copper sulphate, phenol, boric acid, cobalt sulphate, hydrazine sulphate, chloramine T., Carrel-Dakin's solution,⁽¹⁰⁾ etc.

(10) H. D. Dakin, *J. Am. M. A.*, **67** (1916), 1777.

TABLE. Relation between Fungi, Fungicides and the pH of media.

Fungicides	<i>Trichophyton interdigitale</i>	<i>Trichophyton violaceum</i>	<i>Epidemophyton inguinale</i>	<i>Aspergillus oryzae</i>
Boric acid	—	—	1:1,217-740 pH 6.37	1:486-370 pH 5.98
HgI ₂	1:7,200-4,867 pH 6.44	—	1:14,200-7,200 pH 6.52	—
HgCl ₂	—	—	1:12,000-8,110 pH 6.00	1:2,367-1,200 pH 5.31
C ₆ H ₅ OH	1:1,217-925 pH 6.45	—	1:1,217-925 pH 6.45	1:1,217-925 pH 6.45
Salicylic acid	1:1,217-925 pH 5.40-5.00	1:1,217-925 pH 5.40-5.00	1:1,217-925 pH 5.4-5.00	1:750-550 pH 4.17-4.20
Sodium salicylate	—	—	—	1:38-35
Sodium benzoate	—	—	—	1:12-9
C ₆ H ₅ SO ₂ Cl	1:660-536 pH 4.12	—	1:1,286-869 pH 4.62	1:537-452 pH 3.98
Phenylthiourea	1:1,100-800 pH 6.65	1:2,433-1,850	1:1,100-800 pH 6.68	1:293-227 pH 6.60
Thiourea	1:253-195 pH 6.78	—	1:720-487 pH 6.70	1:253-195 pH 6.78
CuSO ₄	1:710-360 pH 4.02	—	—	1:710-360 pH 4.02
Co ₂ (SO ₄) ₃	1:1,286-652 pH 5.64	—	1:1,217-925 pH 5.64	—
Hydrazine sulphate	1:720-487 pH 6.22	—	1:720-487 pH 6.22	—
NaHSO ₃	1:710-360 pH 6.41	—	—	1:710-360 pH 6.41
Al ₂ (SO ₄) ₃	1:243-185 pH 4.39	—	1:360-243 pH 4.73	—
ZnSO ₄	1:710-360 pH 5.77	—	1:360-243 pH 5.64	—
Quinine sulphate	1:410-275 pH 6.20-6.00	—	1:701-334	—
Chloramine T.	1:710-360 pH 6.91	—	1:1,217-925 pH 6.74	1:710-360 pH 6.91
NH ₂ OH·HCl	1:486-370 pH 4.97	—	—	1:710-360
Carrel-Dakin's solution (0.5% sodium hypochlorite)	1:18-12	—	1:18-12	1:9-5
Iodine	—	—	—	1:3,600-2,433
Acetic acid	—	—	—	1:93-75 pH 4.50-4.08
Lactic acid	—	—	—	1:19-15 pH 3.52-3.02
NaC	—	—	—	1:8-5

are of acidic or alkaline character. Therefore when they are added to the medium as described above, the pH is lowered or elevated to a certain degree. For this reason the pH values of the media which prevent the growth or kill fungi are recorded underneath. However the pH values represent approximations only, since they are not determined at a constant temperature but over an interval between 35°C and 45°C.

Addition of fungicide to the medium influences the pH according to the nature of the compound. Certain chemicals as shown on the table do not act merely as fungicides, but their acidity is also responsible for the prevention of the growth of the fungi. This consideration is very important for practical application in chemotherapy.

As is seen in the table, HgI_2 , iodine, HgCl_2 have the highest power as fungicides, and salicylic acid, phenyl-thiourea, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, chloramine T, etc. follow in order. However the effective power of $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, $\text{NH}_2\text{OH}\cdot\text{HCl}$, sulphates, etc. may be due largely to their high acidity. Acetic acid is much more toxic than lactic acid. For example, *Aspergillus oryzae* can not grow in acetic medium at a pH of 4.08 while it grows in lactic medium even at a pH of 3.52. Sodium benzoate is a much weaker fungicide than lactic acid. If it is present in the medium in the ratio of 1:12 or about 8 per cent., *Aspergillus oryzae* will grow upon it. Sodium chloride has the weakest position among the chemicals. That is to say a ratio of about 1:5 or a concentration of 20 per cent. is necessary to prevent the growth of *Aspergillus oryzae*. This is of importance with regard to food preservation. It is interesting to note that thiourea exhibits a definite toxic value for the fungi combined with neutral and harmless properties for human tissue.

Summary.

The effectiveness of various fungicides on *Trichophyton interdigitale*, *Trichophyton violaceum*, *Epidermophyton inguinale*, and *Aspergillus oryzae* was studied, when added to Sabouroud's culture medium, previously adjusted to pH 6.9 (± 2) and containing 0.5 per cent. of sodium chloride.

The results are tabulated giving the concentrations which permitted, and those which prevented, growth. The pH values at the concentration which prevented growth are recorded.

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OLIVE OIL OZONIDE AND ITS FUNGICIDAL QUALITY.*

By Taichi HARADA.

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Ozone has been much used recently not only in the determination of the structure of unsaturated organic compounds, but commercially for sterilization of drinking water in the reservoirs of large cities such as Paris and Petrograd, and in the paint and varnish industries.

The present investigation is concerned with a therapeutic agent for the infectious fungus skin disease, known as ringworm. For this purpose the following conditions, at least, should be satisfied.

First, while the chemically combined ozone must be stable at room temperature, contact with the heat of the human body should cause it to give off sufficient nascent oxygen to destroy the pathogenic micro-organisms.

Second, the compound and its decomposition products as a whole must not have any irritating or harmful effects on a delicate skin or tissue.

Third, the compound must have a moderate oxidizing power combined with a strong penetrating power upon the skin or tissue in which it should remain for some time.

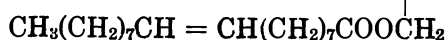
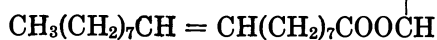
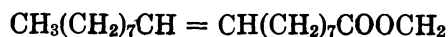
On the basis of these considerations various ozonides of unsaturated fatty acids or their glycerides were roughly studied. However, these substances did not meet fully with the above requirements. The ozonide of olive oil, however, gave a fairly satisfactory result. The effect of ozone upon olive oil was studied by Fenaroli,⁽¹⁾ and Dover and Appleby.⁽²⁾

The compositions of olive oils from different sources are given in Table 1. The linoleic acid glyceride content varies from 0.5 to 7%, sometimes being as high as 17%. The presence, in the oil, of a large amount of linoleic acid or its glyceride is undesirable, since the ozonides of these compounds might decompose easily producing various aldehydes or acids of shorter carbon chains and giving relatively high acidity or low pH to the product as a whole. The acidity thus produced might be irritating or harmful to a delicate skin or tissue. In the present experiment the effective substance in olive oil is the glyceride of oleic acid or triolein which has the following structural formula :

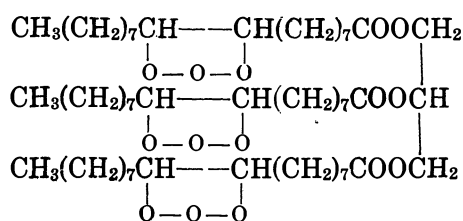
* Patent pending.

(1) *Gazz. Chim. Italiana*, **36**, ii (1906), 292.

(2) *Ind. Eng. Chem.*, **18** (1923), 63.



This combines with three molecules of ozone when brought in contact with it. The double bonds or ethylene linkages of the three oleic acid groups of triolein, take up three molecules of ozone and a definite saturated chemical compound, triolein ozonide, is produced. The structural formula may be represented as follows :



When this ozonide comes in contact with heat it decomposes at the ozone linkages and produces nascent oxygen slowly or rapidly depending upon the degree of heat which is added.

Table 1.
Analysis of Olive Oil.

	California (J. & B.) ⁽¹⁾	Italian (J. & B.) ⁽¹⁾	Spanish (J.) ⁽²⁾		Spanish (T. & S.) ⁽³⁾
Acid value	1.5	—	1.8	Acid value	0.62
Iodine value	85.1	—	83.7	Iodine value	82.7
Sapon. No.	190.0	—	192.4	Sapon. No.	192.6
Olein	84.4	83.1	80.5	Total as oleic acid	83.94
Linolein	4.6	3.9	6.9	„ Linoleic	0.51
Myristin	trace	trace	0.2	„ Glycerol (Calc.)	4.44
Palmitin	6.9	9.2	9.4	„ Palmitic	7.55
Stearin	2.3	2.0	1.4	„ Stearic	2.27
Arachidin	0.1	0.2	0.2	Unsapon. m. and triolein and α-palmitodiolein }	0.79
Unsapon. m.	1.0	1.1	0.8		

(1) G. S. Jamieson and F. W. Banghman, *J. Oil and Fat Ind.*, **2** (1925), 40, 110.

(2) G. S. Jamieson, *J. Oil and Fat Ind.*, **4** (1927), 426.

(3) K. Tafel and J. Sarria, *Chem. Abs.*, **20** (1926), 1723.

To ozonize olive oil, a series of three glass aerating vessels was used, the principal reaction occurring in the first, and the other two serving as auxiliaries to catch excessive ozone. They were half filled with pure olive oil and a current of ozone, washed by passing through a dilute soda solution to remove oxides of nitrogen, was drawn through by means of a sufficiently high vacuum suction. The distinct yellow colour of the oil in the first vessel became pale yellow or nearly colourless at the end of the process. This aeration served not only to remove the volatile aldehydes, or acids which were formed as by-products in the ozonization of the oil, but to maintain the temperature of the whole not higher than the room temperature throughout the operation.

To ozonize, for example, one gallon of olive oil to the saturation point it was necessary to treat the oil far more than 200 hours with a current of about 1.5 grams ozone per hour. It was found that further treatment was a great disadvantage, for the oil became viscous and a white foam resulted. To clear up the foam a few days of standing at room temperature were required.

Table 2.

Changes of Physical and Chemical Constants of Olive
Oil by Ozone Treatment.

Ozone treatment in hours	Increased viscosity at 25°C.	Iodine value	Refractive index at 28°C.	Acid value in KOH mg.	Bleaching time in mins. 10 c.c. of 0.02% indigo carmine solution	Available oxygen after 3 months standing at 25° to 32°C. in %
0	0	85.86	1.4656	1.0	—	—
24	27	78.46	1.4653	4.5	140	0.11
48	73	68.27	1.4653	6.0	37	0.19
72	127	60.83	1.4652	8.7	24	0.23
96	200	55.79	1.4651	13.5	18	—
111	245	53.18	1.4651	13.8	15	—
114	254	53.05	1.4650	13.4	14	—
117	264	53.43	1.4650	13.7	12	—
120	273	53.81	1.4650	13.5	12	0.37
135	318	47.19	1.4650	13.4	11	—
144	345	48.52	1.4652	14.0	9	—
159	382	44.15	1.4653	13.6	9	0.61
164	468	43.40	1.4653	13.9	9	0.64
180	600	38.66	1.4655	17.6	8	0.71
203	855	34.19	1.4659	19.1	13	0.86

Physical and chemical constants of this ozonized oil are related to the time of treatment under the conditions described. As shown in Table 2 the refractive index of the olive oil gradually dropped from 1.4656 to 2.4650 and then rose again to 1.4659 by the passing of ozone for 120 to 203 hours, while its iodine value (this test is not reliable for ozonized oil except as a general index) dropped steadily from 85 to 34. The viscosity and the available oxygen content of the oil increased markedly and in proportion to the time of ozone treatment. The acid value of the oil rapidly increased from 1.0 to 13.5 with 96 hours and then remained constant up to 164 hours of treatment. The acidity was probably due to the presence of the decomposition products of the ozonide of trilinolein. A further increase of acidity by further treatment was probably due to the decomposition products of triolein ozonide.

For the purposes and under the conditions which are described above, it was found sufficient to treat the oil for only about 120 hours. The colour of the product or ozonide thus obtained was pale yellow, but on standing for some days it gradually became colourless. The available oxygen content of this product was found to be about 0.45% of its own weight. This strength is taken as its standard for commercial purposes by the author. The method for the determination of the available oxygen content or of the oxidizing power will be reported in a separate paper.

The product has a slightly bitter taste and an agreeable odour. It is fairly stable at room temperature. For *Staphylo Cocci* the phenol coefficient of the ozonized oil containing 0.37% available oxygen was about 0.05. When 1 c.c. of the product was shaken with 10 c.c. of water, the pH of the aqueous solution was found to be not less than 3.0 at 37°C. The oil itself does not give any irritation even to a delicate skin or tissue.

When the ozonide was brought in contact with human skin or tissue at 37°C. or body temperature it gave off nascent oxygen immediately but moderately. It had strong penetrating but no irritant qualities even for delicate tissue. At the same time it remained for an indefinite period in the oxidizing condition on or in the skin or tissue. Therefore the product might destroy easily pathogenic micro-organisms especially ringworm fungi in skin lesions.

The experimental data on the fungicidal qualities for the fungi, *Trichophyton interdigitale*, *Trichophyton violaceum*, *Epidermophyton inguinale*, and *Aspergillus oryzae* which is abundantly cultured for the diastatic enzyme preparation,⁽³⁾ are represented in Table 4, including a comparison with the common oxidizing agents, namely hydrogen peroxide, and sodium hypochlorite which is sold under the name Zonite.

(3) T. Harada, *Ind. Eng. Chem.*, **23** (1931), 1434.

Table 3.

Stability of Olive Oil Ozonide.

Time in hours	At 25 to 32°C gas formed in c.c. by decomposition in the presence of light*	Available oxygen in per cent.	At 8-10°C gas formed in c.c. by decomposition*	Available oxygen in per cent.
0	0	0.48	0	0.48
3	5	0.44	0	—
12	21	0.42	0	0.48
21	32	0.40	?	—
35	41	0.40	—	0.48

* The top lip of a burette was suspended so that it touched the bottom of a beaker containing the ozonide and the burette was filled with 60 c.c. of the ozonide. The figures are empirical values which do not represent the gas formed by decomposition of 60 c.c. of the ozonide, for as the gas is formed and rises in the burette, an equal volume of the oil flows out into the beaker.

Table 4.

Fungicides and Fungi.

Oxidizing agents	Available oxygen in per cent.	<i>T. inter-digitale</i>	<i>T. violaceum</i>	<i>E. inguinale</i>	<i>A. oryzae</i>
H ₂ O ₂	1.04	1:71 - 36	—	1:24 - 15	1:8 - 5.6
NaOCl	0.28	1:24 - 18	—	1:19 - 15	1:8 - 5.6
Olive oil ozonide	0.37	1:360-180	1:360-263	1:180-121	1:28-15

The figures in Table 4 are ratios of the agent concentrations to the amounts of the medium. The figures at the left indicate the concentrations at which the fungi grew while the figures at the right indicate the concentrations too high for specific fungus growth. The technique of the experiments is reported in a previous paper.

It is suggested that olive oil ozonide has not only fungicidal, antiseptic, and germicidal qualities, but a remarkable property as the healing and soothing remedy for the eczema caused by ringworm infection and the like.* Moreover at the same time, it restores poisoned and oxygen-starved cells to a normal condition by its production of nascent oxygen.

* This clinical problem is being carried on in co-operation with Dr. D. Stetson of Roosevelt Hospital, New York, N.Y.

Summary.

The requirements which a pathogenic fungicide must satisfy for use on human skin or tissue are pointed out. The ozonide of olive oil was prepared and examined in these respects with fairly satisfactory results. Changes in physical and chemical constants produced by ozone treatment of olive oil are given.

Certain qualities of the ozonide with regard to its fungicidal effect for ringworm are discussed.

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DETERMINATION OF THE OXIDIZING POWER OF AVAILABLE OXYGEN OF THE PEROXIDE AND THE OZONIDE OF AN OIL OR FAT.

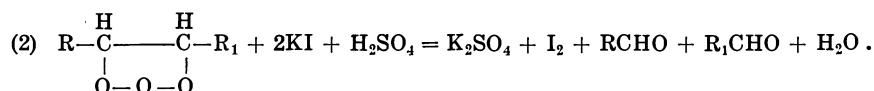
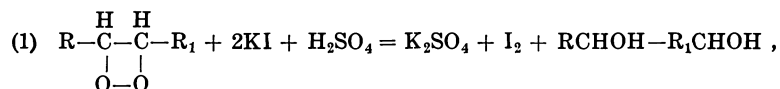
By Taichi HARADA.

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The usual Kingzett method of determining ozone and hydrogen peroxide is not suitable for the peroxide or ozonide of an oil or fat, because the oxygenated oil or fat is insoluble in water. The method is so slow as to prohibit its employment for routine work. The method presented here was devised by the author to be applicable to oils and fats.

Exactly one cubic centimeter measured by a pipett graduated in tenths of a cubic centimeter, or more accurately, exactly one gram, of oxygenated oil or fat is placed in an Erlenmeyer flask, or a cylinder, of 250 c.c. capacity. Under constant shaking, 20 c.c. of a 10% solution of potassium iodide and 3 c.c. of a 20% solution of sulphuric acid are added, the free iodine produced is titrated with a 0.1 N solution or more accurately with a 0.01 N solution, of sodium thiosulphate, and then the flask is heated in a boiling water bath. The further developed iodine is then titrated with the thiosulphate solution using a starch solution as the indicator. This procedure is repeated until no more iodine is set free by the decomposition of the sample.

The principle of this method is based on the following chemical reactions :



The available oxygen content is calculated as in the case of hydrogen peroxide or ozone. One cubic centimeter of 0.1 N sodium thiosulphate solution is equivalent to 0.0127 gr. of iodine which is equivalent to 0.0008 gr. of oxygen. If one gram of olive oil ozonide, for example, requires 4.7 c.c. of a 0.1 N sodium thiosulphate solution for the liberated iodine, then, its oxidizing power or available oxygen content is given in per cent. by weight as follows :

$$\frac{4.7 \times 0.0008 \times 100}{1} = 0.375\%$$

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ON THE HEATS OF FUSION OF TITANIUM TETRA-
CHLORIDE, CARBON TETRACHLORIDE, AND
ANTIMONY PENTACHLORIDE.

By Nobuyuki NASU.

Received April 5th, 1934. Published April 28th, 1934.

The present writer recently determined the freezing point curves of the binary systems of titanium tetrachloride, carbon tetrachloride, and antimony pentachloride, but he did not carry out his experiment with the solutions sufficiently dilute to calculate the heats of fusion of these chlorides. Hence the freezing points of these systems were determined again with sufficiently dilute solutions and the heats of fusion were calculated by the following formula :

$$\ln \frac{N}{N'} = \frac{Q}{R} \left\{ \frac{1}{T'} - \frac{1}{T} \right\}^{(1)},$$

where T and T' are the freezing points of the solutions with the concentrations N and N' , respectively. It must be mentioned here that the above formula is applicable only to the case where the two components do not form a solid solution.

Experimental.

The apparatus used was exactly the same as described in the previous paper.⁽²⁾ In the present experiment, a mixture of solid carbon dioxide and ether was used as a cooling agent, and since a small quantity of solute had to be accurately measured, a special burette, in which 0.01 c.c. corresponded to 2 mm. in length, was used. An example of cooling curves is shown in Fig. 1.

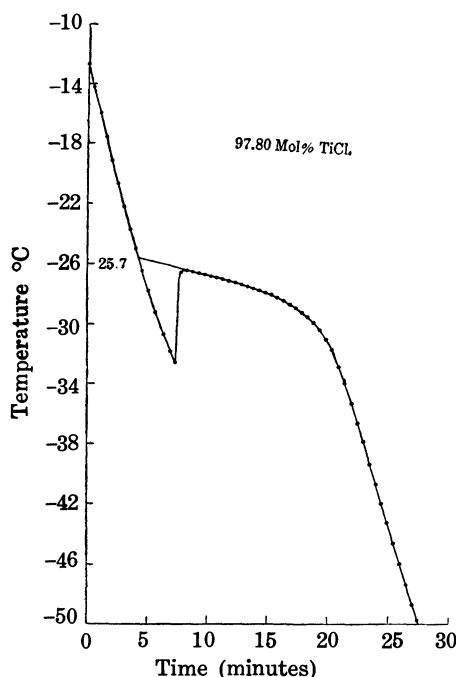


Fig. 1. An Example of Cooling Curves ($\text{TiCl}_4\text{--CCl}_4$)

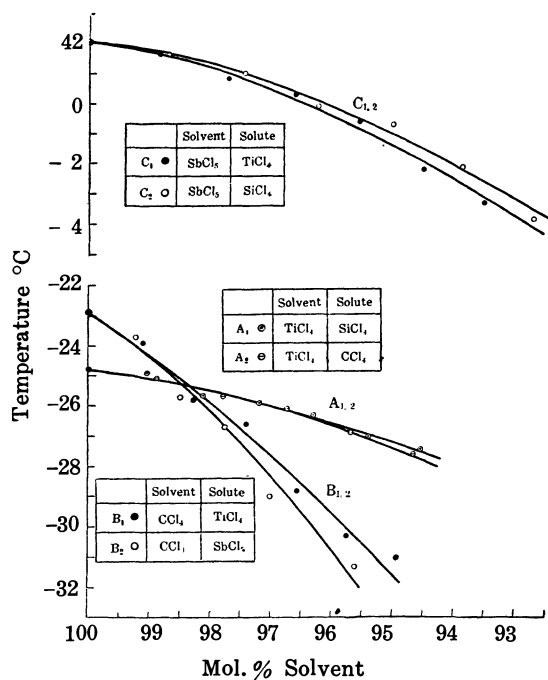


Fig. 2.

(1) S. Mitsukuri and A. Nakatsuchi, *Sci. Rep.*, **15** (1926), 50.

(2) This Bulletin, **8** (1933), 195.

(1) TiCl_4 . The freezing point-concentration curves of the solution containing SiCl_4 and CCl_4 as the solute respectively are marked with

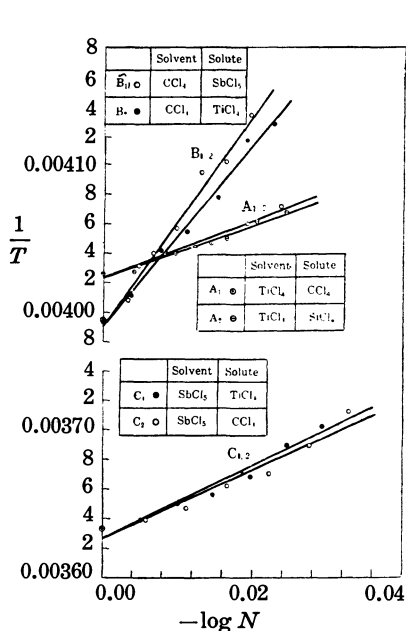


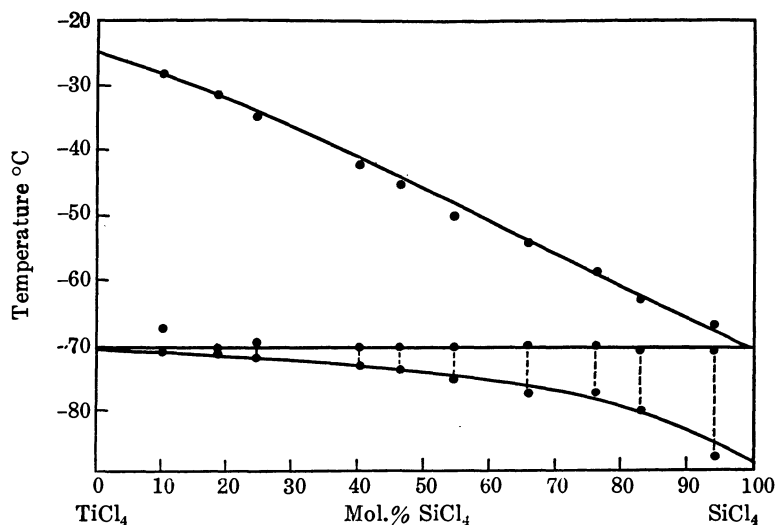
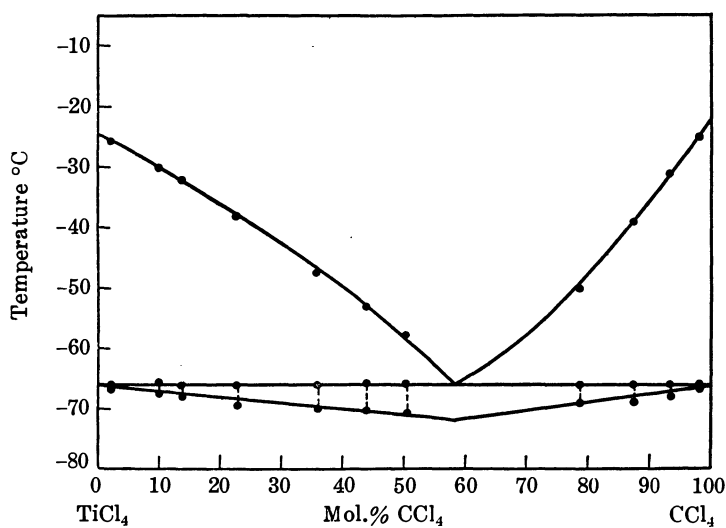
Fig. 3.

tion used in the former investigation being 10.3 mol. % for SiCl_4 and 6.3 mol. % for CCl_4 . Hence in order to confirm this point, a differential thermal analysis was carried out. In the system $\text{TiCl}_4\text{-CCl}_4$, the eutectic horizontal could be traced up to 2.2 mol. %, but in the system $\text{TiCl}_4\text{-SiCl}_4$, the same line could not be detected below the concentration of 10.3 mol. % SiCl_4 . Again, the reaction time of eutectic obtained in the former experiment is plotted against the temperature as shown in Fig. 4 and 5 from which it is concluded that the system $\text{TiCl}_4\text{-SiCl}_4$ or $\text{TiCl}_4\text{-CCl}_4$ does not form solid solution on TiCl_4 -rich side. The formula of the freezing point depression can thus be applied to the calculation of the heat of fusion of the compounds.

(2) CCl_4 . The heat of fusion of CCl_4 was likewise calculated from the data obtained from dilute solutions containing CCl_4 as the solvent and TiCl_4 and SbCl_5 as the solute, respectively. The results are shown in Table 2 and by curves $B_{1,2}$ in Fig. 2 and 3. The values calculated from the above results for CCl_4 , TiCl_4 and SbCl_5 being used as the solute, are respectively 740 and 630 cal./mol., thus giving the mean value of 680 cal./mol. or 4.40

$A_{1,2}$ in Fig. 2, and the $\frac{1}{T} - \ln N$ curve is almost straight as shown by $A_{1,2}$ in Fig. 3. The heat of fusion Q was calculated by taking two points on this straight line, which was drawn by the method of the least square. The values of Q corresponding to two solutes SiCl_4 and CCl_4 were found to be 2520 and 2350 cal./mol. respectively, the mean of which is 2440 cal./mol. or 12.90 cal./gr.

The formula for the depression of freezing point is applicable, as stated before, only when one of the two components does not show any solubility in the other in solid state. In the determination of the freezing point diagram of the system $\text{TiCl}_4\text{-SiCl}_4$, it was not ascertained whether the solid TiCl_4 is soluble in SiCl_4 or CCl_4 , the lowest concentra-

Fig. 4. TiCl_4 - SiCl_4 .Fig. 5. TiCl_4 - CCl_4 .

cal./gr. It is also necessary to confirm if solid carbon tetrachloride is soluble in TiCl_4 or SbCl_5 .

In the system CCl_4 - TiCl_4 , the eutectic horizontal can be traced down to 1.79% TiCl_4 by a differential thermal analysis as shown in Table 4. It is found from Fig. 5 that in the system CCl_4 - TiCl_4 no solution seems to exist on CCl_4 -rich side.

In the former investigation, the freezing point curve of the system $\text{CCl}_4\text{-SbCl}_5$ was not determined, and hence the question as to the existence of solid solution on CCl_4 -rich side remains untouched; but from the concordant results in the calculation of the heats of fusion of CCl_4 from the data obtained with TiCl_4 or SbCl_5 as the solutes, it is concluded that solid CCl_4 has no solubility in SbCl_5 .

(3) SbCl_5 . In this case TiCl_4 and CCl_4 were used as solutes. The results of experiments are given in Table 3 and shown by curves $C_{1,2}$ in Fig. 2 and 3. The heats of fusion of SbCl_5 calculated from the data obtained with TiCl_4 and CCl_4 as the solutes are 1870 and 1970 cal./mol. respectively, the mean value being 1920 cal./mol. or 6.40 cal./gr. It was also confirmed that in the system $\text{SbCl}_5\text{-TiCl}_4$, solution in solid phase does not exist at all (Fig. 6).

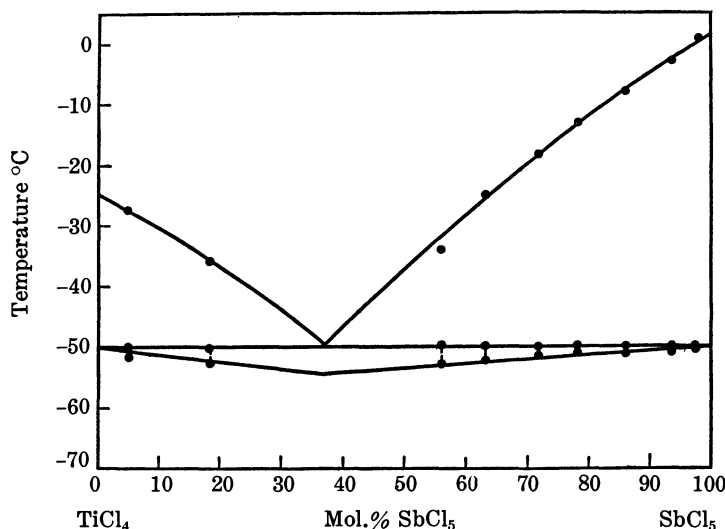


Fig. 6. $\text{TiCl}_4\text{-SbCl}_5$.

Although the freezing point curves of the system $\text{SbCl}_5\text{-CCl}_4$ was not determined in the recent investigation as stated in paragraph (2), it is apparent from the concordant result in the calculation of the heats of fusion of SbCl_5 from the cases where TiCl_4 and CCl_4 are used as solutes respectively that it can be assumed that solid SbCl_5 has no solubility in these two compounds.

The heats of fusion of three chlorides obtained by the present writer and those by previous workers are put together in Table 5 for comparison.

Table 1.

(A) Solvent : TiCl_4 ; Solute : SiCl_4

Mol. % TiCl_4 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-\text{°C}$	T		
100.00	24.8	248.4	0.004026	0.00000
99.05	24.9	248.3	0.004027	0.00415
98.12	25.7	247.5	0.004040	0.00825
97.20	25.9	247.3	0.004044	0.01233
96.30	26.3	246.9	0.004050	0.01637
95.42	27.0	246.2	0.004062	0.02036
94.55	27.4	245.8	0.004068	0.02434

 $Q = 2520$ cal./mol.(B) Solvent : TiCl_4 ; Solute : CCl_4

Mol. % TiCl_4 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-\text{°C}$	T		
100.00	24.8	248.4	0.004026	0.00000
98.89	25.1	248.1	0.004031	0.00485
97.80	25.7	247.5	0.004040	0.00966
96.74	26.1	247.1	0.004047	0.01439
95.69	26.9	246.3	0.004060	0.01913
94.68	27.6	245.6	0.004072	0.02374

 $Q = 2350$ cal./mol. mean $Q = 2440$ cal./mol. or 12.90 cal./gr.Table 2. (C) Solvent : CCl_4 ; Solute : TiCl_4

Mol. % CCl_4 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-\text{°C}$	T		
100.00	22.9	250.3	0.003995	0.00000
99.12	23.9	249.3	0.004011	0.00384
98.26	25.8	247.4	0.004042	0.00762
97.41	26.6	246.6	0.004055	0.01140
96.57	28.0	245.2	0.004078	0.01516
95.75	30.3	242.9	0.004117	0.01886
94.94	31.0	242.2	0.004128	0.02225

 $Q = 740$ cal./mol.

(D) Solvent : CCl_4 ; Solute : SbCl_5

Mol. % CCl_4 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-\text{°C}$	T		
100.00	22.9	250.3	0.003995	0.00000
99.24	23.7	249.5	0.004008	0.00331
98.50	25.7	247.5	0.004040	0.00656
97.76	26.7	246.5	0.004057	0.00984
97.04	29.0	244.2	0.004095	0.01305
96.32	29.4	243.8	0.004102	0.01628
95.62	31.3	241.9	0.004134	0.01945

$Q = 630$ cal./mol. mean $Q = 680$ cal./mol. or 4.40 cal./gr.

Table 3. (E) Solvent : SbCl_5 ; Solute : TiCl_4

Mol. % SbCl_5 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	°C	T		
100.00	2.0	275.2	0.003634	0.00000
98.85	1.6	274.8	0.003939	0.00512
97.73	0.8	274.0	0.003650	0.00997
96.64	0.3	273.5	0.003656	0.01484
95.57	-0.6	272.6	0.003668	0.01968
94.53	-2.2	271.0	0.003690	0.02443
93.51	-3.3	269.4	0.003705	0.02914

$Q = 1870$ cal./mol.

(F) Solvent : SbCl_5 ; Solute : CCl_4

Mol. % SbCl_5 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	°C	T		
100.00	2.0	275.2	0.003634	0.00000
98.71	1.6	274.8	0.003639	0.00564
97.45	1.0	274.2	0.003647	0.01122
96.23	0.1	273.1	0.003662	0.01669
95.03	0.7	272.5	0.003670	0.02214
93.87	-2.1	271.1	0.003689	0.02747
92.73	-3.8	269.4	0.003712	0.03278

$Q = 1970$ cal./mol. mean $Q = 1920$ cal./mol. or 6.40 cal./gr.

Table 4.

Results of the differential thermal analysis.

System	Concentration	Liquidus point °C	Eutectic point °C
TiCl ₄ —CCl ₄	2.20 mol. % CCl ₄ .	—25.5	—65.5
TiCl ₄ —CCl ₄	1.74 mol. % TiCl ₄ .	—25.4	—66.0
TiCl ₄ —SbCl ₅	97.73 mol. % SbCl ₅ .	1.4	—50.9

Table 5. Heat of fusion (cal. per gram)

	TiCl ₄	CCl ₄	SbCl ₅
Values obtained by the author	12.90	4.40	6.40
Those by previous workers	11.70 ⁽³⁾	4.20 ⁽³⁾	8.18 ⁽⁴⁾

As is found from Table 5, the heats of fusion of TiCl₄ and CCl₄ obtained by the present writer and those determined calorimetrically by previous workers are in good agreement, but in the case of SbCl₅, the discrepancy is considerable. The origin of the values, 8.18 cal./gr. adopted by W. Herz is not given in his paper, and hence the exact method of determination can not be known.

Summary.

The heats of fusion of TiCl₄, CCl₄, and SbCl₅ were calculated from the data of the depression of freezing point in dilute solutions. The heats of fusion of TiCl₄, CCl₄ and SbCl₅ were found 12.90, 4.40, and 6.40 cal. per gram respectively. These values were in a close agreement with those observed by previous investigators.

In conclusion the writer wishes to express his hearty thanks to Prof. K. Honda, the President of the Tôhoku Imperial University and to Prof. K. Iwasé for their kind guidances during the course of this work.

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(3) W. H. Latimer, *J. Am. Chem. Soc.*, **44** (1922), 90.

(4) W. Herz, *Z. anorg. allgem. Chem.*, **170** (1928), 237.

THE COLLOIDAL BEHAVIOUR OF SERICIN. I.

By Hideo KANEKO.

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Introduction.

The crude silk fiber spun by the silk-worm, consists of a filament of fibroin surrounded by a glue-like coating known as sericin. Sericin, also called silk-glue, is one of the proteins secreted from the silk gland by the silk-worm. It swells in cold water, and is readily soluble when boiled. The relative proportion of these two components, fibroin and sericin in crude silk differs considerably with different varieties of cocoons, but generally sericin occupies about 25 per cent. of the raw fiber. Mulder gave formula $C_{15}H_{25}N_5O_8$ to sericin, the elementary composition being C : 43, H : 6, N : 16, and O : 35 per cent.

Sericin is commonly accompanied by small amounts of colouring and mineral matters as well as of fatty and waxy substances. The physico-chemical behaviours of sericin have a great influence on the facility in reeling the raw silk from cocoons. For this reason I have studied some colloidal properties of sericin in its various states and varieties.

To the chemical investigation of silk fiber, especially of the amino acids obtained from it, R. Inoue⁽¹⁾ has contributed, and according to his estimation the percentages of the known constituents of silk-glue are as follows :

	Inner layer (per cent.)	Outer layer (per cent.)
Glycocoll	5.77	2.99
Alanine	8.49	9.24
Tyrosine	5.25	2.85
Serine	2.56	6.33
Phenylalanine	2.66	2.60
Leucine	0.73	2.30
Proline	0.35	—
Aspartic acid	6.81	2.74
Glutamic acid	—	0.94

(1) R. Inoue, *Reports Seric. and Silk Ind. Science*, 1929.

E. Hiratsuka⁽²⁾ studied completely the properties of liquid silk in the silk-worm. We shall understand by "fine structure" the molecular and micellar constitution of the proteins as revealed or indicated by chemical investigations, by X-ray spectroscopy, and by other investigations.

It is confirmed by the chemical investigations of Fischer that the proteins consist of long chain-like molecules of condensed or peptide amino acids. The natural proteins consist of more or less uniformly oriented crystallites of parallel polypeptide-type chains. Brill (1923),⁽³⁾ Herzog and Jancke (1927)⁽⁴⁾ state that, under X-ray investigation, fibroin has a crystalline character and that it is a mixture of at least one crystalline and several amorphous compounds, the nature of the mixture varying with the sources of the silk.

Meyer and Mark (1928)⁽⁵⁾ believe that fibroin consists of four principal valence chains of glycyl-alanine, the length of the micellæ being 150 A. U. and corresponding to a polypeptide of at least twenty glycylalanyl groups. But very little work has been conducted to elucidate the chemical constitution of sericin and it is generally believed that it has an amorphous structure. To the study of its chemical composition Abderhalden and his co-workers⁽⁶⁾ have made much contribution. Karrer made a fermentative investigation on fibroin and examined the partial decomposition of sericin by the proteolytic enzymes secreted by some bacteria. E. Furuya has been studying along a similar line in our college. I report here a study of some colloidal behaviours of sericin existing on the cocoon layer and separated from it by boiling in water or by precipitation with an electrolyte.

PART I.

Sec. I. The Solubility of Sericin on the Cocoon Layer.

(1) **The Solubility of Sericin in Water.** Generally, "kaijo" of cocoons is represented by the weight of raw silk reeled per hour under the same condition. The state and colloidal properties of the sericin particles of the cocoon change in a remarkable manner with the external factors during their gelatinization, drying process or their preservation, and the internal

(2) E. Hiratsuka, *Bull. Imperial Seric. Exp. Station, Japan*, Vol. **1** (1918), 203-224.

(3) Brill, "Ein Beitrag zur chem. Konstitution des Seidenfibroins," 1923; *Naturwissenschaften*, **18** (1930), 622.

(4) Herzog and Jancke, *Z. Physik*, **3** (1920), 196; *Helvetica Chim. Acta*, **11** (1928), 529.

(5) Meyer and Mark, *Ber.*, **61** (1928), 1982; *Z. physik. Chem.*, **2** (1929), 115.

(6) Abderhalden, *Z. physiol. Chem.*, **178** (1928), 253; *ibid.*, **207** (1932), 141-146; *ibid.*, **210** (1932), 246; *Biochem. Z.*, **211** (1929), 395; *ibid.*, **226** (1930), 209.

conditions of the liquid silk. It will, therefore, lead to the different solubilities of sericin in water.

R. Inoue⁽⁷⁾ measured already "kaijo" of cocoons by obtaining the curves of the amounts of nitrogen dissolved into the solution in a definite time. Further, he and T. Watanabe found that sericin on the outer layer of cocoons was more soluble in water than that on the inner layer. I confirmed fully their results and further found that the sericin solution obtained from cocoons having good "kaijo" or from the outer layer of cocoons had a stronger power of gelatinization and that this would lead to difficult conglomeration at the contact point of silk fiber on the cocoon.

When the cocoon layer containing the natural sericin is boiled with some distilled water in a flask with a reflux condenser, the sericin particles mostly disperse into the solution and form a hydro-philic colloid containing very small amounts of fatty and colouring matters.

The natural sericin is apt to denature to some extent by heat, alcohol, dialysis, and other external factors, so I used the sericin solution in that condition as the material to be examined. In general the solubility of sericin in water varies with the kinds of cocoons, with its total amounts existing on the cocoon fibers, with the amount of salts in water, and also with the temperature of the water.

The sericin is not a simple compound, but a mixture of similar proteins as described later. By the difference in the proportions of the mixtures in compliance with varieties of cocoons, the solubility in water will be affected, because each component has a different solubility in water.

The author determined some physico-chemical properties of aqueous solutions of the cocoon layer and observed that the solubility of sericin particles in dilute solutions is proportional to their relative viscosities, indices of refraction, or lowering of surface tension, and that the logarithm of solubility is also proportional to turbidity.

From these relations I was able to determine the solubility of sericin by measuring its physico-chemical properties. As already described, the solubility of sericin on the cocoon layer varies with its "kaijo." This will be caused mostly by the different proportions of two kinds of sericin, but it will also be affected by the different pH values of sericin solutions.

I have determined electrically the pH values of the sericin solutions, allowing them to stand for two hours after preparation. The results are shown in Table 1.

(7) R. Inoue, *Rep. Seric. and Silk Ind. Science*, **1** (1926), Vol. 1.

Table 1,

Cocoons having good "kaijo"		Cocoons having middle "kaijo"		Cocoons having bad "kaijo"	
conc. (%)	pH	conc. (%)	pH	conc. (%)	pH
0	4.88	—	—	—	—
0.05	4.96	0.07	5.09	0.07	4.92
0.09	5.70	0.10	5.29	0.11	5.09
0.11	5.79	0.14	5.38	0.14	5.30
0.16	5.89	0.16	5.81	0.16	5.62
0.20	5.96	0.19	5.86	0.24	5.73
0.26	6.01	0.22	5.97	0.29	5.78
0.35	6.21	0.31	6.05	0.38	5.98
0.40	6.20	0.42	6.11	0.48	6.08

Though the *pH* value of the sericin solution is a function of its concentration, a solution from cocoons having better "kaijo" shows the greater value in the same concentration. In order to clarify the cause of this difference of *pH* I made the following experiment.

A diaphragm with 0.1 g. cocoon layer was made at the middle point of an U-tube, 20 c.c. of distilled water free from carbon dioxide were poured into it, then the platinum electrodes were inserted at the ends of the tube, and an electric current of 110 volts was passed through. After an hour *pH* of each solution around the electrodes was measured.

The cathodic solution showed weak basicity (*pH* 7.43–7.81) and the anodic moderate acidity (*pH* 3.37–3.73). I detected qualitatively a minute amount of ammonia in the cathodic solution, and glycoll, tyrosine, bitartrate, etc. in the anodic solution. It seemed to me that these compounds existed originally in the cocoon layer before the electric treatment and caused the change of *pH*.

Even for the same cocoon *pH* values of the solutions obtained by boiling it with water vary with the position of the layers.

The outer cocoon layer showed generally the greatest *pH* value, next the inner layer, and the middle layer the smallest, the difference in the values for these layers depending on "kaijo" of the cocoon. The swelling and the solubility of sericin increased greatly with the rise in temperature and two cases are expressed by the same equation.

$$W \times 100 = S = At^K \quad (A = 1.0),$$

where W represents the quantity of dissolved sericin in g. when 5 g. cocoons are boiled with 100 c.c. of distilled water in a flask for 30 minutes, t the temperature in centigrade, A and K constants.

The value of constant K depends not only on the temperature, but also on "kaijo" of the cocoon (Table 2).

Table 2.

"kaijo"	$K(20-50^{\circ}\text{C.})$	$K(60-90^{\circ}\text{C.})$	$K(100^{\circ}\text{C.})$
good	0.55	0.85	0.84
middle	0.43	0.71	0.77
bad	0.42	0.67	0.75

This leads to the conclusion that the sericin dispersed from the cocoon fibers having good "kaijo" contains more sericin A which is comparatively easily soluble even in cold water. And at the neighbourhood of 60°C. the solubility of sericin, that is constant K , increases rapidly.

2. **The Solubility of the Natural Sericin in Salt Solutions.** The neutral salts have generally a solvent action on proteins and under nearly all conditions exert a recognizable influence on proteins in solution. Denis (1856) noticed that the solubility of a certain protein increased by the addition of neutral salts and it is also known that in dilute solutions (less than 2 or 3 normal) neutral salts of the alkalies, or of alkali earth metals, increase the solubility of the protein in water. Cohen (1924) showed that the rate at which solubility is raised by increasing quantities of a salt is characteristic of each individual protein, and gave formula $S/S_0 = \alpha\mu^{\beta}$, where S_0 is the solubility of the protein in water, S the solubility in a salt solution with an ionic strength μ , α and β constants.

A. A. Green (1931)⁽⁸⁾ also examined the solubility of hæmoglobin in salt solutions and showed that the solubility in concentrated solutions at constant pH and temperature was represented by an equation of the type:

$$\log S = \beta - K'_s \mu,$$

where S is the solubility, μ the ionic strength, β an intercept constant which in the case of non-electrolytes is $\log S_0$, and K'_s the salting out con-

(8) A. A. Green, *J. Biol., Chem.*, **93** (1931), 495-541; *ibid.* **95** (1932), 47-66.

stant apparently independent of temperature and of pH but varying with salts. He obtained later the following experimental equation:

$$\log S - 1.6\sqrt{C} = 1.30 - k_0C,$$

where C is the concentration of the salt and k_0 is a constant which varies with electrolytes.

The solubility of sericin on the cocoon in dilute salt solutions has been qualitatively investigated by R. Inoue⁽⁹⁾ and he showed that the solubility of sericin increased in the presence of a small amount of salts (chlorides, sulphates, carbonates, etc.) and, on the contrary, decreased in concentrated salt solutions.

I also examined the solubility of sericin on the cocoon in salt solutions and obtained the following data: Cocoon layer 2.2 g. (Nichi 110 $\times$ Shi 103, 1931) were boiled with 100 c.c. of distilled water in a flask with a reflux condenser for 30 minutes, the solution was filtered, and then the solubility of sericin was estimated by the determination of nitrogen contained in the filtrate.

$\log (S/S_0)$ is not proportional to the square root of concentration, $\sqrt{C}$, but it decreases gradually with increasing salt concentration.

$$\frac{\log (S/S_0)}{\sqrt{C}} + K_0C = \text{const.} = K \text{ or } \log (S/S_0) + K_0C^{\frac{3}{2}} = K\sqrt{C},$$

where S is the solubility of sericin in pure water, K_0 and K constants.

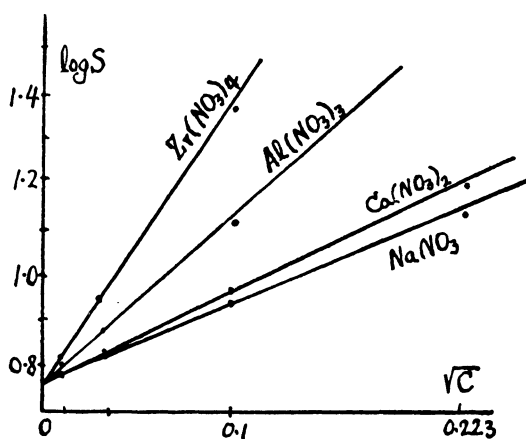


Fig. 1.

(9) R. Inoue, loc. cit.

The value of constant K depends on the nature of the cation of the inorganic salt, and it increases with increasing valency of the cation (Table 3 and Fig. 1).

Table 3

Nitrate	K	K_0	Chloride	K	K_0
NaNO_3	1.86	4	NaCl	1.85	10
$\text{Ca}(\text{NO}_3)_2$	2.11	4	CaCl_2	2.34	20
$\text{Al}(\text{NO}_3)_3$	6.00	50	AlCl_3	5.93	60
$\text{Zr}(\text{NO}_3)_4$	7.58	50	—	—	—

Solutions of sodium salts of organic acids

	K	K_0		K	K_0
Formate	1.74	2	Oleate	4.52	4
Acetate	1.75	2	Benzoate	1.65	2
Propionate	1.72	2	Benzene-sulphonate	1.60	2
Butyrate	1.715	2	Bitartrate	1.63	2
Valerate	1.706	2	Citrate	2.50	2

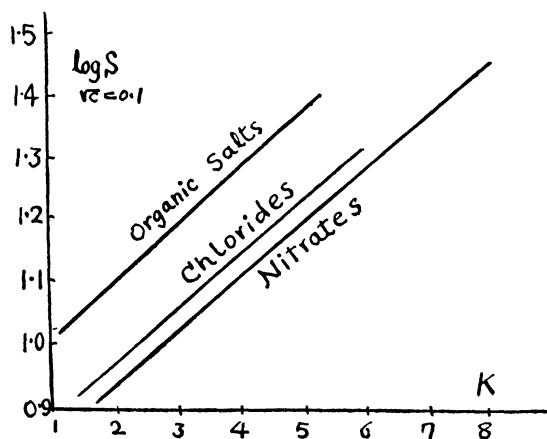


Fig. 2

The solubility of sericin increases in the presence of small amounts of nitrates, chlorides, or sodium salts of organic acids, and the relation

between the solubility and the concentration is expressed by the same equation :

$$\log \frac{S}{S_0} + K_0 C = K.$$

At the same salt-concentration the values of constant K for salts used are proportional to the logarithm of the solubility of sericin as shown in Fig. 2. In the case of the sodium salts of lower fatty acids the solubility of sericin diminishes slightly with increasing number of carbon atoms in the molecule. The sodium salts of organic acids have stronger dispersing power for sericin than those of inorganic acids and the effect of anions of sodium salts on the solubility of sericin is reversed to the effect of anions on the solubility of fibroin (chloride < bitartrate < acetate < citrate).

Sec. II. The Relative Viscosity of Colloidal Solutions of Sericin.

There is one property in which hydrophilic colloids like sericin sol differ characteristically from water which acts as their dispersion medium. That is viscosity, and it is found that it increases with, but at a greater rate than, the concentration, showing that there is always some association.

For the measurement of the relative viscosity I used the well known Ostwald viscosimeter with a capillary tube of the inner diameter 0.08 cm.

The sericin sol was obtained by boiling about 5 g. of cocoon layers with 200 c.c. of distilled water in a flask with a reflux condenser for 30 minutes. After filtration it was immediately cooled to 20°C. in cold water, and then I measured its relative viscosity after leaving it to stand at 20°C. for 15 minutes.

(1) **Variation of Viscosity with Concentration.** The viscosities of sericin sols at varying concentrations are shown in Table 4. All these viscosities are expressed in the term of the viscosity of water at 20°C. which is taken as unity.

The slope of the viscosity-concentration curve as shown in Fig. 3 is an indication of the extent to which association between the solute and the solvent has occurred. The rise in viscosity with increasing concentrations is very rapid in solutions of sericin. The viscosity-concentration constant K or $\frac{\ln \eta_r}{C}$ is not strictly constant and increases gradually with increasing concentration of sericin and is given by the equation $K = aC + b$, where a and b are constants. But K can be considered to be constant in a narrow range of concentration.

Table 4
Relative Viscosity at 20°C., (good "kaijo").

Conc. C (g./100 c.c.)	flow. time t (sec.)	rela. visz. $\eta_r = \frac{td}{t_0d_0}$	visc.-conc. const. $\frac{\ln \eta_r}{C} = K$
0.59	10.34	1.320	$0.2043 \times 2.3 = 0.4699$
0.47	9.74	1.233	0.1935 „ = 0.4451
0.40	9.47	1.185	0.1843 „ = 0.4239
0.38	9.40	1.171	0.1804 „ = 0.4149
0.30	9.00	1.122	0.1666 „ = 0.3832
0.28	9.05	1.115	0.1638 „ = 0.3882
0.107	8.40	1.037	0.1474 „ = 0.3380
0.00	8.12	1.000	—

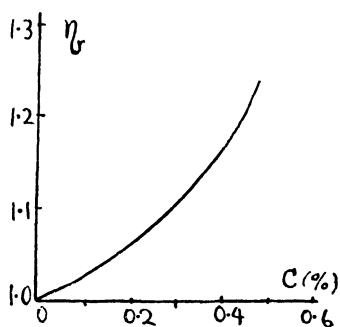


Fig. 3.

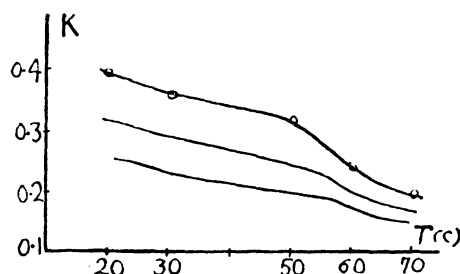


Fig. 4.

Sericin forms molecular aggregates in the aqueous solution and the value of the viscosity coefficient is a function of the volume of the molecular aggregates. For the polymeric organic materials Duclaux proposed the following equation :

$$M = \frac{\ln \eta_r}{C} \times 10^4 = K \times 10^4,$$

where M is the molecular weight of a polymeric material. Staudinger gave the following equation :

$$M = \frac{1}{K_{cm}} \cdot \frac{\ln \eta_r}{C} = \frac{K}{K_{cm}},$$

where K_{cm} is the molecular weight-concentration constant having a mean value 5×10^{-4} .

$$M = \frac{1}{5} K \times 10^4 \quad (M > 50000)$$

If the equation of Duclaux holds also for sericin sol, its molecular weight would be 4026 in concentration of about 0.35 per cent. This molecular weight is ten times as great as the value calculated for the empirical formula $C_{15}H_{25}N_5O_8$ (= 403.0) of Bowmann.

Table 5.

	a	b	α	$M(C = 0.35\%)$
good "kaijo"	0.2711	0.310	0.0735	4026
middle "	0.2544	0.230	0.0647	3320
bad "	0.2075	0.161	0.0431	2382

$$\frac{\ln \eta_r}{C} = aC + b, \quad \frac{\ln \eta_r}{C\left(C + \frac{b}{a}\right)} = a^2 = a$$

It can be seen from Table 5 that the degree of aggregation of sericin particles obtained from a cocoon having good "kaijo" is greater than that of sericin micellæ obtained from a cocoon having bad "kaijo."

Though the calculated molecular weight depends on the diameter of capillary tube of the viscosimeter used, all correspond nearly to $403n$, where n may be any integer.

Staudinger considered that such an anomalous increase of viscosity would be due to the existence of long chain particles.

Fikentscher⁽¹⁰⁾ recently proposed an equation containing a single arbitrary constant, which, although empirical, appears to be superior in general applicability to any hitherto used, namely

$$\frac{\ln \eta_r}{C} = \frac{ak^2}{1+bkC} + k,$$

where C is the concentration in grams per 100 c.c. of the solution, a , b , and k constants, the last constant k being the arbitrary one, which

(10) H. Fikentscher and H. Mark, *Kolloid-Z.* **49** (1929), 135.

Fikentscher calls "Eigenviskosität." The values of constant k obtained from his equation for hydroxydecanoic acid polymeride are shown in Table 6.

Table 6.

mol. wt.	k	mol. wt.	k
780	0.020	9330	0.058
1710	0.025	16900	0.071
5670	0.042	20600	0.081

Table 7.

temp. (C.)	good "kaijo"			middle			bad		
	C	K	k_p	C	K	k_p	C	K	k_p
20	0.34	0.4025	0.067	0.34	0.3144	0.059	0.33	0.227	0.049
30	0.35	0.3536	0.063	0.34	0.2860	0.055	0.33	0.246	0.051
50	0.34	0.3200	0.060	0.33	0.239	0.051	0.32	0.211	0.044
60	0.34	0.2301	0.049	0.32	0.202	0.046	0.34	0.188	0.044
70	0.33	0.1925	0.045	0.35	0.1535	0.039	0.38	0.132	0.036

(k_p proper viscosity).

Both the viscosity-concentration constant K and proper viscosity k_p decrease with rising temperature (Table 7) and the value of $\frac{dK}{dt}$ changes suddenly near 60°C. as shown in Fig. 4. As already described sericin forms molecular aggregates in association with water molecules and this tendency to aggregate diminishes as temperature rises.

The value of K or k_p for sericin obtained from cocoons having good "kaijo" is always larger than that for sericin obtained from cocoons having bad "kaijo."

The sericin sol which has been obtained from cocoons having good "kaijo" and will have larger aggregation and higher hydration is more easily influenced by the temperature change. The solvation volumes of 1 g. sericin, b , calculated from Fikentscher's formula, are also a function of temperature (Table 8). B is the degree of solvation and is equal to b/v , where v is the specific volume.

Table 8.

temp. (C.)	good "kaijo"			middle			bad		
	<i>C</i>	<i>b</i>	<i>B</i>	<i>C</i>	<i>b</i>	<i>B</i>	<i>C</i>	<i>b</i>	<i>B</i>
20	0.34	16.2	21.22	0.34	12.6	16.44	0.33	8.1	10.53
30	0.34	14.0	18.34	0.35	12.1	15.79	0.32	8.5	11.05
50	0.36	13.4	—	0.36	9.2	—	0.36	7.1	—
60	0.33	8.2	—	0.36	8.5	—	0.36	7.7	—
70	0.32	6.5	—	0.33	5.2	—	0.33	4.1	—

It can be presumed that above 60°C. the sol form of sericin is present, while below 20°C. the gel form occurs. Between these temperatures both forms will be present in a ratio depending on the temperature and the age of the solution. Hardy considered that the ionized protein had a greater effect on the viscosity of water than the unionized, and, with Pauli and Samec (1909), he attributed this to a greater association between the ionized protein and water.

2. **Variation of Viscosity with Time.** The viscosity of the sericin solutions in which the formation of colloidal micellæ occurs is not constant, but changes with time, showing there is a gradual change in structure. The increase of viscosity of sericin solutions with time, which ultimately leads to gelatinization, is probably due to separation of finely dispersed precipitate throughout the system.

The effect of time on viscosity is the greatest between 20° and 60°C.. Below 20°C., or above 50°C., the variation of viscosity with time is very small for a few hours (Table 9).

Table 9.

time	0°C.	10°C.	20°C.	50°C.	70°C.
(min.)	0.35 %	0.32 %	0.32 %	0.27 %	0.43 %
15	22.21	12.35	9.07	5.94	5.98
30	21.93	12.30	9.36	6.09	6.04
45	21.73	12.50	9.45	6.30	6.17
60	21.64	12.43	9.47	6.66	6.20
120	22.50	12.45	9.50	8.96	6.17
180	22.89	12.50	9.28	9.80	6.23

Above 60°C. the curve runs practically parallel to the time axis; at lower temperatures, an increase in viscosity with the time is clearly noticed. (Fig. 5).

3. Variation of Viscosity with Time and Temperature.

In making a solution of sericin by heating cocoons in distilled water, the sericin dissolved entirely in sol form, which was cooled immediately, and viscosity measurements were made after 15 minutes.

The logarithm of flowing time in sec. of sericin solutions is a linear function of the logarithm of temperatures in centigrade; $\ln t = \ln \alpha - \beta \ln T$ or $t = \alpha T^{-\beta}$, where α and β are constants (Table 10).

Table 10.

"kaijo"	α	β	conc.
good	14.1	0.20	0.45%
middle	12.2	0.18	0.26%
bad	12.2	0.18	0.28%

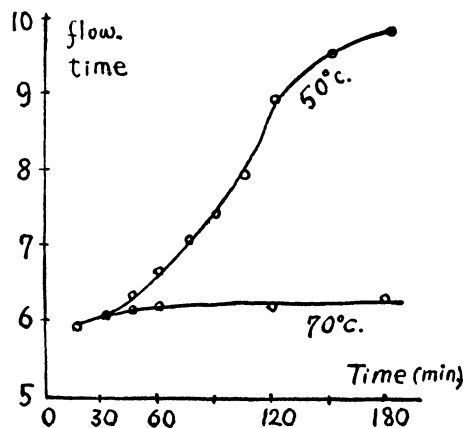


Fig. 5.

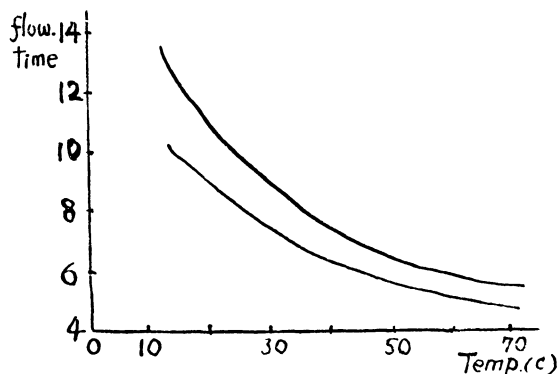


Fig. 6.

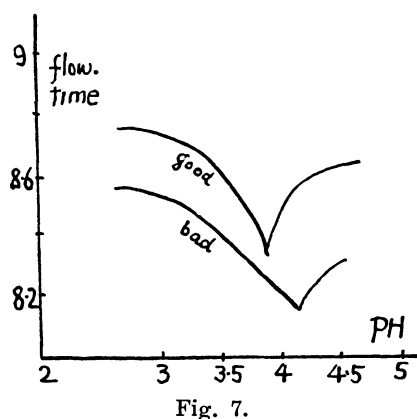
Constant α depends on the concentration of the sericin solution and constant β on the aggregation of sericin particles.

4. Effect of Acids and Alkalis on the Viscosity. The condition in which sericin dissolves has a considerable effect on the viscosity of the solution. At the isoelectric point the charge of sericin particles is zero, and, since the electro-viscous effect is necessarily minimum at this point, the viscosity must increase both with an increase and with a decrease of the hydrogen-ion exponent.

The relation between the viscosity and hydrogen-ion concentration are shown in Table 11.

Table 11.
Effect of HCl, (at 20°C.).

good (0.185 %)		mid. (0.20%)		bad (0.175 %)	
flow. time	pH	flow. time	pH	flow. time	pH
8.65	4.665	8.50	4.50	8.29	4.40
8.55	4.060	8.44	4.26	8.21	4.29
8.52	4.025	8.31	4.18	8.20	4.25
8.50	3.985	8.26	4.12	8.16	4.175
8.31	3.960	8.25	4.00	8.31	3.73
8.62	3.520	8.51	3.58	8.34	3.68
8.75	2.810	8.68	2.78	8.50	2.77
8.82	2.450	8.73	2.37	8.58	2.27



The influence of hydrogen-ion concentration on the viscosity of sericin is reproduced in Fig. 7. As shown in Table 11 the pH value has a much marked effect on the viscosity, the viscosity coefficient for 0.2 per cent. solution of sericin rising from 8.5 at pH 4.0 to 8.82 at pH 2.45. The point of minimum viscosity in sericin coincides with the isoelectric point.

For sericin sol the hydrogen-ion concentration of the isoelectric point varies with the concentration of the protein (Table 12).

Table 12.
Isoelectric point of sericin.

"kaijo"	0.2 %	0.12 %
good	3.95	3.80
middle	4.12	3.97
bad	4.18	4.08

Table 13.

vol. added in c.c.	0.1N NaOH	0.1N NH ₄ OH
	0.22 %	0.29 %
0	1.080	1.110
0.05	1.130	1.130
0.1	1.105	1.183
0.2	1.085	1.210
0.3	1.071	1.225

The isoelectric point of sericin obtained from cocoons having good "kaijo" is always more acidic than that of sericin obtained from cocoons having bad "kaijo." The viscosity of sericin in alkaline solution increases with the concentration of alkali and attains to the maximum point and falls again with increased hydroxyl-ion activity (Table 13).

5. **Effect of Inorganic Salts on the Viscosity.** I investigated the effect of inorganic salts which are commonly contained in small amounts in the natural water on the viscosity of the sericin solution (Table 14).

Table 14.

(10 c.c. sericin solution + x c.c. salt solution + $(2-x)$ c.c. water).

$\frac{N}{100}$ salt solution added in c.c. x	0.08 per cent. sericin solution (at 20°C), flowing time in sec.				
	NaCl	KNO ₃	MgCl ₂	CaCl ₂	FeCl ₃
0	9.7	9.7	9.7	9.7	9.7
0.1	9.8	9.2	10.2	10.4	10.0
0.3	9.8	9.3	10.8	10.5	10.2
0.5	10.1	9.6	11.2	10.8	10.6
0.7	10.4	10.0	11.6	10.6	11.0
0.9	10.8	10.2	11.8	10.4	10.9
1.1	10.9	10.5	12.2	10.3	10.6
1.5	12.0	10.7	13.5	10.2	10.6

When potassium nitrate is added to a sericin solution there is first a decrease in the viscosity. When more of the salt is added the viscosity continually increases. In the case of calcium chloride and ferric chloride the effect on the viscosity is contrary to the case of potassium nitrate. The viscosity, after passing through a maximum, goes on decreasing. When sodium chloride or magnesium chloride is added to the same solution the viscosity increases with increasing concentration of the electrolyte (Fig. 8).

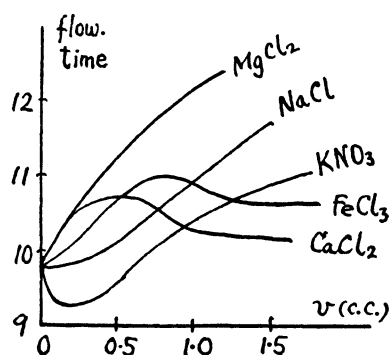


Fig. 8.

SUR L'ÉQUILIBRE HÉTÉROGÈNE DU SYSTÈME TERNAIRE DES COMPOSÉS ORGANIQUES.

Par Tei-ichi ASAHINA.

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Une méthode simple d'analyse thermique a été proposée, il y a une dizaine d'années, par M. H. Rheinboldt,⁽¹⁾ et a trouvé généralement son usage dans l'étude des composés moléculaires organiques surtout réalisée par cet auteur, par M. P. Pfeiffer et par leurs élèves.⁽¹⁾ Nous l'avons aussi utilisée et elle nous a donné de bons résultats.⁽²⁾ Elle n'a le plus souvent été appliquée jusqu'ici qu'aux systèmes binaires, mais on peut raisonnablement l'appliquer aux systèmes ternaires des composés organiques et, généralement, à tous les composés dont les points de fusion sont relativement bas. Cette application a été tentée et nous a donné de bons résultats que nous rapportons ci-dessous. Un des buts de cette étude est la recherche de composés moléculaires ternaires nouveaux. Comme exemple de cette tentative, le système: β -naphthol, méthylènedioxybenzal-acétophénone et acide picrique a été étudié. On savait déjà qu'il y a formation de composés moléculaires entre la méthylènedioxybenzal-acétophénone et l'acide picrique (le rapport moléculaire étant 1:2)⁽³⁾ et aussi entre le β -naphthol et l'acide picrique (la proportion moléculaire étant 1:1)⁽⁴⁾ mais cette formation n'avait jamais été observée entre le β -naphthol et la chalcone.⁽³⁾

Premièrement nous avons fait les trois diagrammes d'équilibre hétérogène correspondants aux trois systèmes binaires. (Voyez les tables 1-3 et les figures 1-3). Ensuite nous avons préparé plusieurs mélanges d'acide picrique et de naphthol en diverses proportions et nous avons cherché l'état d'équilibre entre chacun d'eux et la chalcone, les températures de dégel et de congel étant données dans les tables 4-12 et les figures 4-12.

(1) P. Pfeiffer "Organische Molekülverbindungen," 1927, 66-85.

(2) *Acta Phytochimica*, **7** (1933), 187; Ce bulletin, **9** (1934), 131 et 181.

(3) Ce bulletin, **9** (1934), 131.

(4) Ce système a été étudié par M. B. Kuriloff, les compositions des mélanges étant exprimées en mol-pourcentages. Nous avons répété l'expérimentation d'après notre méthode et nous avons trouvé qu'il y a un peu de discordance entre ses données et les nôtres. Voyez *Z. physik. Chem.*, **23** (1897), 673; **24** (1897), 441; et aussi C. Marchetti; *Gazz. chim. ital.*, **12** (1882), 503.

Table 1. (Voyez la Fig. 1.)

constituants du système				températures	
acide picrique		β -naphthol		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.	—	100.0	—	—	121.5
10.0	0.0300	90.0	0.2700	109.0	117.0
20.0	0.0400	80.0	0.1600	109.2	115.2
30.0	0.0600	70.0	0.1400	109.3	133.5
40.0	0.0800	60.0	0.1200	108.0	145.5
50.0	0.1200	50.0	0.1200	111.0	153.0
60.0	0.1659	40.0	0.1106	135.0	156.3
70.0	0.1400	30.0	0.0600	109.5	154.0
80.0	0.1600	20.0	0.0400	109.2	142.5
90.0	0.1800	10.0	0.0200	109.0	121.5
100.0	—	0.0	—	—	122.0

Table 1a. (d'après M. Kuriloff.)

constituants du système				mol. % d' acide picrique	points de fusion
acide picrique		β-naphthol			
%	g.	%	g.		°C.
0	—	100.0	—	0	121.0
7.5	0.0916	92.5	1.1266	4.87	117.0
18.4	0.3714	81.6	1.6494	12.4	127.0
32.4	0.4978	67.6	1.0387	23.1	136.4
46.4	0.5106	53.6	0.5914	35.2	150.8
61.3	2.2615	38.7	1.4267	49.9	157.0
61.3	0.8675	38.7	0.5449	50.0	157.0
62.6	0.7330	37.4	0.4363	51.4	156.4
72.8	3.1089	27.2	1.1634	62.9	151.0
78.8	2.2878	21.2	0.6158	70.2	146.0
90.3	2.3769	9.7	0.2552	85.4	120.2
90.9	3.1089	9.1	0.3095	86.4	118.0
97.2	2.2296	2.8	0.0647	95.6	117.0
100.0	—*	0.0	—*	100. *	122.2

*Les chiffres des ces colonnes sont ceux qui ont été donnés en pourcentages moléculaires par M. Kuriloff. Nous les donnons dans les première et troisième colonnes convertis en pourcentages en poids.

Table 2. (Voyez la Fig. 2.)

constituants du système		températures	
méthylènedioxychalcone	β -naphthol	points de dégel	points de congel
% 0,0 10,4 20,0 30,0 40,0 50,0 60,0 70,0 75,0 80,0 85,0 90,0 95,0 100,0	g. — 0,0021 0,0040 0,0060 0,0080 0,0100 0,0120 0,0140 0,0150 0,0160 0,0170 0,0180 0,0190 —	% 100,0 89,6 80,0 70,0 60,0 50,0 40,0 30,0 25,0 20,0 15,0 10,0 5,0 0,0	g. — 0,0180 0,0160 0,0140 0,0120 0,0100 0,0080 0,0060 0,0050 0,0040 0,0030 0,0020 0,0010 —
		°C. — 72,0 72,0 71,0 72,0 71,0 71,0 71,0 71,5 71,0 72,0 71,5 72,0 —	°C. 121,5 116,5 111,5 104,5 95,5 83,8 80,0 95,5 100,5 106,6 110,8 114,5 118,4 121,0

Table 3. (Voyez la Fig. 3.)

constituants du système		températures	
méthylènedioxychalcone	acide picrique	points de dégel	points de congel
% 0,0 2,7 4,8 10,0 14,2 21,3 24,7 25,0 34,1 40,6 52,6 64,1 70,0 80,0 85,0 90,0 95,0 100,0	g. — 0,0011 0,0010 0,0010 0,0010 0,0016 0,0020 0,0050 0,0030 0,0041 0,0050 0,0066 0,0140 0,0160 0,0170 0,0180 0,0190 —	% 100,0 97,3 95,2 90,0 86,8 78,7 75,3 75,0 65,9 59,4 47,4 35,9 30,0 20,0 15,0 10,0 5,0 0,0	g. — 0,0400 0,0200 0,0090 0,0060 0,0059 0,0061 0,0150 0,0058 0,0060 0,0045 0,0037 0,0060 0,0040 0,0030 0,0020 0,0010 —
		°C. — 113,5 113,5 113,5 113,5 113,5 113,5 113,0 114,5 104,5 105,0 104,0 104,0 104,3 103,5 104,0 104,5 —	°C. 122,0 120,0 116,5 119,8 123,0 126,5 127,2 127,3 128,5 128,0 125,3 117,5 111,0 110,0 113,5 116,5 119,0 121,0

Table 4. (Voyez la Fig. 4.)

constituants du système				températures	
acide picrique 10% + β-naphthol 90%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
4.0	0.0006	96.0	0.0144	92.1	118.5
20.0	0.0030	80.0	0.0120	68.3	106.5
26.8	0.0044	73.2	0.0120	67.0	99.0
38.0	0.0057	62.0	0.0093	69.0	85.5
50.0	0.0065	50.0	0.0065	70.0	75.5
65.0	0.0130	35.0	0.0070	69.5	94.2
79.0	0.0120	21.0	0.0032	69.8	106.0
88.8	0.0135	11.2	0.0017	71.0	112.3
100.0	—	0.0	—	109.0	117.0

Table 5. (Voyez la Fig. 5.)

constituants du système				températures	
acide picrique 20% + β-naphthol 80%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	68.0	114.5
20.0	0.0030	80.0	0.0120	68.0	106.5
30.0	0.0045	70.0	0.0105	67.0	97.0
44.0	0.0066	56.0	0.0084	67.5	82.5
50.0	0.0070	50.0	0.0070	70.0	79.0
60.0	0.0090	40.0	0.0060	68.5	94.0
80.0	0.0120	20.0	0.0030	70.0	110.0
100.0	—	0.0	—	109.2	115.2

Table 6. (Voyez la Fig. 6.)

constituants du système				températures	
acide picrique 30% + β-naphthol 70%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	68.0	116.2
20.0	0.0030	80.0	0.0120	70.0	108.0
34.0	0.0051	66.0	0.0099	70.0	95.0
42.0	0.0063	58.0	0.0087	69.0	85.0
54.0	0.0081	46.0	0.0069	70.0	99.0
60.0	0.0090	40.0	0.0060	69.5	107.0
70.0	0.0105	30.0	0.0045	70.0	118.5
84.0	0.0126	16.0	0.0024	70.0	127.0
100.0	—	0.0	—	109.3	133.5

Table 7. (Voyez la Fig. 7.)

constituants du système				températures	
acide picrique 40% + β-naphthol 60%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	69.8	115.3
20.0	0.0030	80.0	0.0120	70.0	108.2
30.0	0.0045	70.0	0.0105	70.0	100.0
40.0	0.0040	60.0	0.0060	69.5	91.0
50.0	0.0070	50.0	0.0070	70.0	102.0
70.0	0.0105	30.0	0.0045	69.5	127.0
80.0	0.0120	20.0	0.0030	70.0	136.0
90.0	0.0135	10.0	0.0015	70.0	142.2
100.0	—	0.0	—	108.0	145.5

Table 8. (Voyez la Fig. 8.)

constituants du système				températures	
acide picrique 50% + β-naphthol 50%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	73.0	115.5
20.0	0.0030	80.0	0.0120	70.5	110.0
30.0	0.0045	70.0	0.0105	70.0	100.5
40.0	0.0080	60.0	0.0120	70.0	91.2
50.0	0.0060	50.0	0.0060	68.5	104.5
60.0	0.0090	40.0	0.0060	69.0	120.5
70.0	0.0105	30.0	0.0045	69.0	133.0
79.5	0.0120	20.5	0.0031	69.0	140.0
90.0	0.0135	10.0	0.0015	69.5	148.0
100.0	—	0.0	—	111.0	153.0

Table 9. (Voyez la Fig. 9.)

constituants du système				températures	
acide picrique 60% + β-naphthol 40%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	85.5	115.5
20.0	0.0030	80.0	0.0120	84.5	109.3
30.0	0.0045	70.0	0.0105	84.0	102.0
40.0	0.0060	60.0	0.0090	84.5	93.2
50.0	0.0105	50.0	0.0105	85.0	105.5
60.0	0.0090	40.0	0.0060	84.0	119.5
70.0	0.0105	30.0	0.0045	84.0	132.0
80.0	0.0120	20.0	0.0030	84.0	139.0
90.0	0.0135	10.0	0.0015	81.5	149.0
100.0	—	0.0	—	135.0	156.3

Table 10. (Voyez la Fig. 10.)

constituants du système				températures	
acide picrique 70% + β-naphthol 30%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	85.0	117.0
20.0	0.0030	80.0	0.0120	85.0	110.0
30.0	0.0045	70.0	0.0105	84.0	105.1
40.0	0.0060	60.0	0.0090	82.0	101.0
50.0	0.0070	50.0	0.0070	84.1	106.0
59.2	0.0090	40.8	0.0062	84.0	114.5
70.0	0.0105	30.0	0.0045	84.3	127.5
77.9	0.0120	22.1	0.0034	83.0	135.2
90.0	0.0135	10.0	0.0015	102.5	144.0
100.0	—	0.0	—	109.5	154.0

Table 11. (Voyez la Fig. 11.)

constituants du système				températures	
acide picrique 80% + β-naphthol 20%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	86.0	117.0
20.0	0.0030	80.0	0.0120	85.0	110.0
30.0	0.0045	70.0	0.0105	83.0	104.0
40.0	0.0060	60.0	0.0090	84.5	108.0
50.0	0.0070	50.0	0.0070	83.5	114.0
59.6	0.0090	40.4	0.0061	85.2	116.0
69.5	0.0105	30.5	0.0046	84.5	116.0
79.5	0.0120	20.5	0.0031	101.5	126.0
90.0	0.0135	10.0	0.0015	101.5	134.0
100.0	—	0.0	—	109.2	142.5

Table 12. (Voyez la Fig. 12.)

constituants du système				températures	
acide picrique 90% + β-naphthol 10%		méthylènedioxy- chalcone		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
10.0	0.0015	90.0	0.0135	83.0	117.0
20.0	0.0030	80.0	0.0120	83.0	110.0
30.0	0.0045	70.0	0.0105	84.5	106.0
40.0	0.0060	60.0	0.0090	83.0	114.0
50.0	0.0070	50.0	0.0070	82.0	120.0
60.0	0.0090	40.0	0.0060	84.0	123.0
70.0	0.0105	30.0	0.0045	102.0	122.2
79.5	0.0120	20.5	0.0031	102.0	119.5
89.4	0.0135	10.6	0.0016	104.5	113.5
96.0	0.0144	4.0	0.0006	102.0	117.0
100.0	—	0.0	—	109.0	121.5

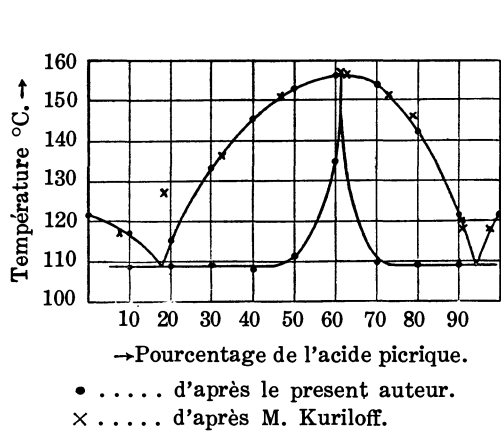


Fig. 1.

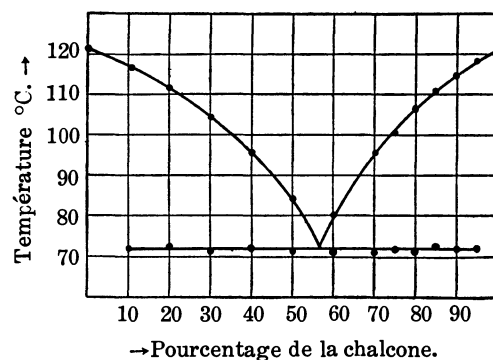


Fig. 2.

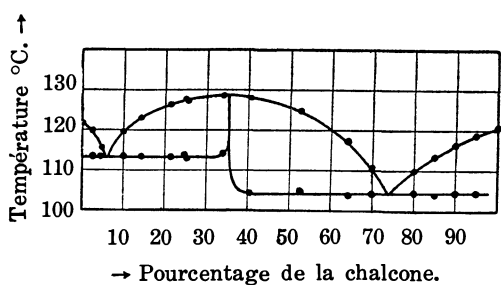


Fig. 3.

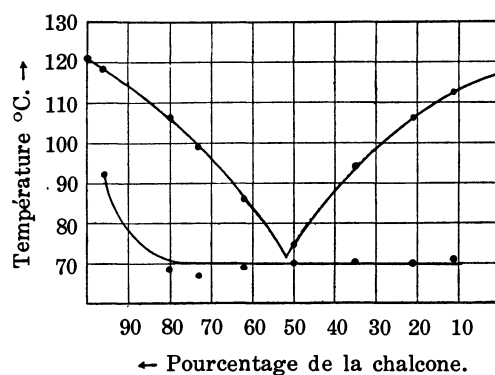


Fig. 4.

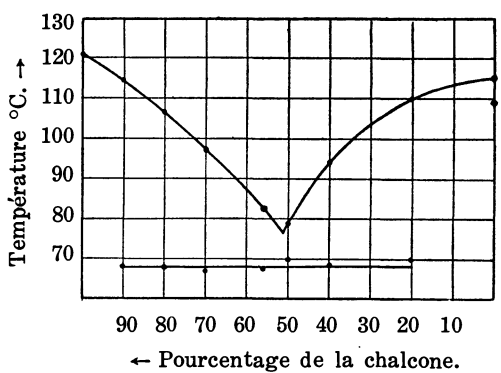


Fig. 5.

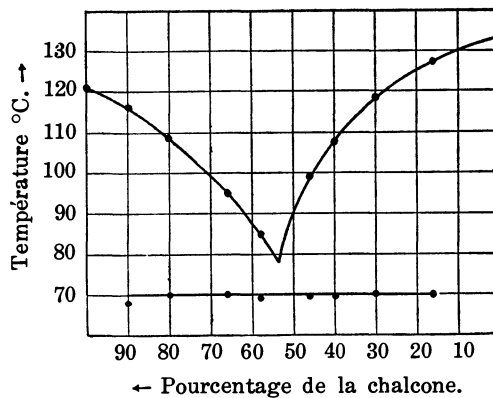


Fig. 6.

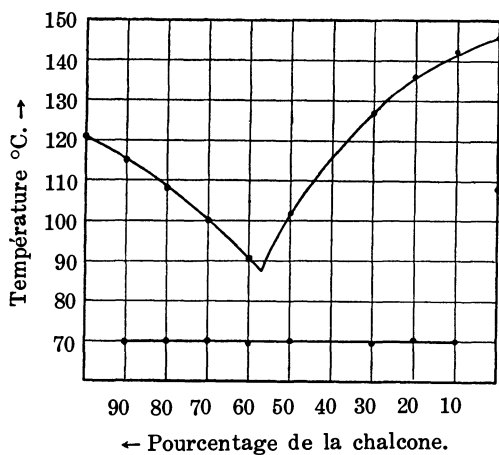


Fig. 7.

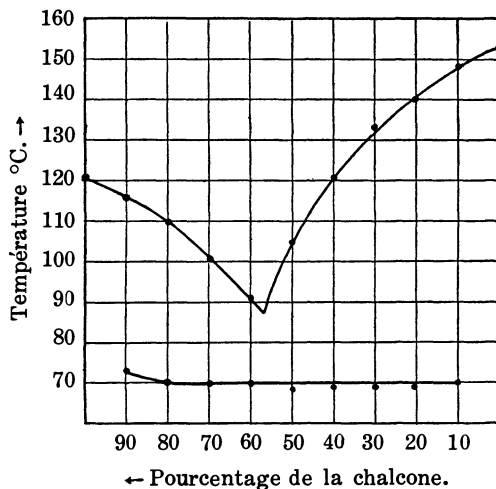


Fig. 8.

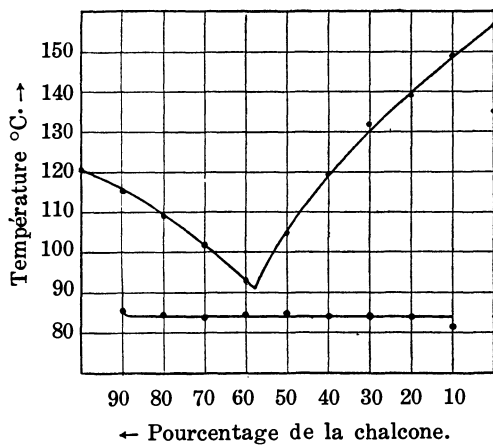


Fig. 9.

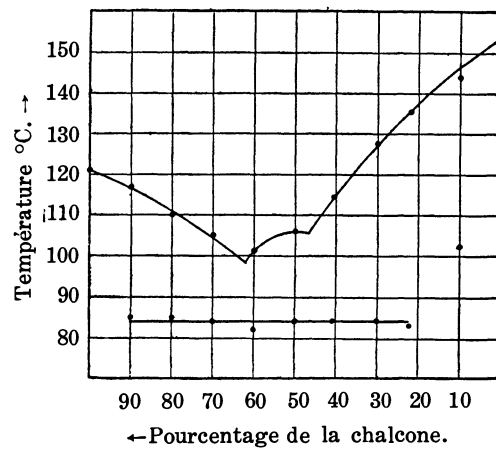


Fig. 10.

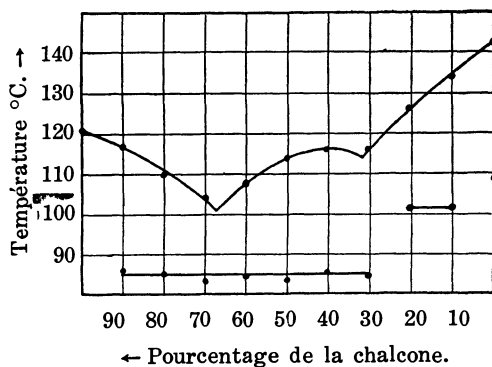


Fig. 11.

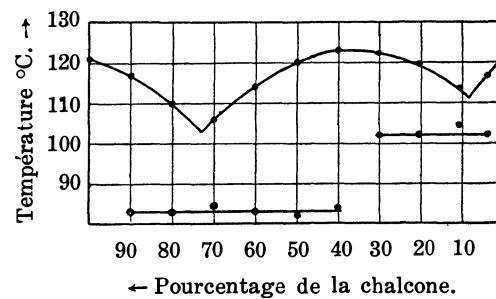


Fig. 12.

Par interpolation dans les 12 diagrammes, on peut trouver le pourcentage correspondant à chaque point de congel. On peut ainsi faire des isothermes de cinq en cinq degrés et obtenir un diagramme d'équilibre hétérogène du système ternaire. (Fig. 21.)

Toutefois, pour les réaliser complètement, il a fallu préciser leur valeur dans le domaine voisin de 100% d'acide picrique. On a fait quelques mesures additionnelles qui sont indiquées ci-dessous. (Voyez les tables 13-19 et les figures 13-19). Dans la figure 20, on donne les lignes, le long desquelles toutes les observations mentionnées ont été rapportées. La figure 21 est le diagramme complète d'équilibre hétérogène des phases solides et liquides du système ternaire. Il montre clairement d'une part qu'il n'y a pas de formation de composé moléculaire, et d'autre part que ce système ternaire présente trois points eutectiques.

Table 13. (Voyez la Fig. 13.)

constituants du système				températures	
acide picrique 90% + méthylènedioxy- chalcone 10 %		acide picrique 90% + β -naphthol 10%		points de dégel	points de congel
%	g.	%	g.	°C.	°C.
0.0	—	100.0	—	—	121.0
20.0	0.0030	80.0	0.0120	102.5	113.0
30.0	0.0030	70.0	0.0070	102.0	111.0
40.0	0.0060	60.0	0.0090	103.0	110.5
50.0	0.0050	50.0	0.0050	103.0	112.0
60.0	0.0090	40.0	0.0060	102.5	112.0
70.0	0.0070	30.0	0.0030	102.5	113.0
79.0	0.0120	21.0	0.0032	102.5	113.0
100.0	—	0.0	—	113.5	119.8

Table 14. (Voyez la Fig. 14.)

Le mélange de méthylènedioxychalcone 20% et β -naphthol 80% A.

Le mélange de méthylènedioxychalcone 20% et acide picrique 80% B.

A	B	A : B	températures	
			points de dégel	points de congel
g. sans le B	g. —	—	°C.	°C.
0.0140	0.0020	7 : 1	72.0	111.5
0.0120	0.0040	6 : 2	68.0	105.0
0.0100	0.0060	5 : 3	70.0	117.0
0.0080	0.0080	4 : 4	68.0	130.0
0.0060	0.0100	3 : 5	69.0	139.0
0.0040	0.0120	2 : 6	89.0	139.5
0.0020	0.0140	1 : 7	102.5	130.0
—	sans l'A	—	104.0	117.0
			113.5	125.7

Table 15. (Voyez la Fig. 15.)

Le mélange de méthylènedioxychalcone 40% et β -naphthol 60% A.

Le mélange de méthylènedioxychalcone 40% et acide picrique 60% B.

A	B	A : B	températures	
			points de dégel	point de cngel
g. sans le B	g. —		°C.	°C.
0.0110	0.0010	5.5 : 0.5	72.0	95.5
0.0100	0.0020	5 : 1	69.5	90.0
0.0100	0.0050	4 : 2	70.0	91.0
0.0080	0.0080	3 : 3	70.0	109.0
0.0040	0.0080	2 : 4	69.0	120.5
0.0020	0.0100	1 : 5	88.2	117.0
0.0010	0.0110	0.5 : 5.5	87.0	120.5
—	sans l'A		87.0	124.5
			104.5	128.3

Table 16. (Voyez la Fig. 16.)

Le mélange d'acide picrique 70% et β -naphthol 30% A.

Le mélange d'acide picrique 70% et méthylènedioxychalcone 30% B.

A	B	A : B	températures	
			points de dégel	points de cngel
g. sans le B	g. —		°C.	°C.
0.0500	0.0100	5 : 1	109.5	154.0
0.0500	0.0250	4 : 2	102.3	147.0
0.0600	0.0600	3 : 3	103.0	136.5
0.0300	0.0600	2 : 4	102.2	126.0
0.0100	0.0500	1 : 5	103.0	116.2
—	sans l'A		103.5	124.0
			113.7	129.0

Dans les trois tables 17—19, on met

le mélange d'acide picrique 70% + β -naphthol 30% X.

le mélange d'acide picrique 70% + méthylènedioxychalcone 30% Y.

Table 17. (Voyez la Fig. 17.)

Le mélange de X : Y = 4 : 2 A.

Acide picrique B.

A	B	A : B	températures	
			points de dégel	points de cngel
g. sans le B	g. —		°C.	°C.
0.0100	0.0020	5 : 1	103.0	136.5
0.0080	0.0040	4 : 2	103.0	133.0
0.0060	0.0060	3 : 3	103.3	127.0
0.0040	0.0080	2 : 4	103.5	118.2
0.0020	0.0100	1 : 5	103.5	111.0
—	sans l'A		103.2	117.5
				122.0

Table 18. (Voyez la Fig. 18.)

Le mélange de $X:Y=3:3$ A.

Acide picrique B.

A	B	A : B	températures	
			points de dégel	points de congel
g. sans le B	g. —		°C.	°C.
0.0100	0.0020	5 : 1	102.2	126.0
0.0080	0.0040	4 : 2	103.0	123.0
0.0060	0.0060	3 : 3	103.0	116.0
0.0040	0.0080	2 : 4	103.0	108.5
0.0020	0.0100	1 : 5	102.5	111.5
—	sans l'A			117.0
				122.0

Table 19. (Voyez la Fig. 19.)

Le mélange de $X:Y=2:4$ A.

Acide picrique B.

A	B	A : B	températures	
			points de dégel	points de congel
g. sans le B	g. —		°C.	°C.
0.0100	0.0020	5 : 1	103.0	116.2
0.0100	0.0050	4 : 2	103.0	116.0
0.0060	0.0060	3 : 3	103.2	115.5
0.0040	0.0080	2 : 4	103.2	113.0
0.0020	0.0100	1 : 5	103.0	113.0
—	sans l'A		103.0	117.5
				122.0

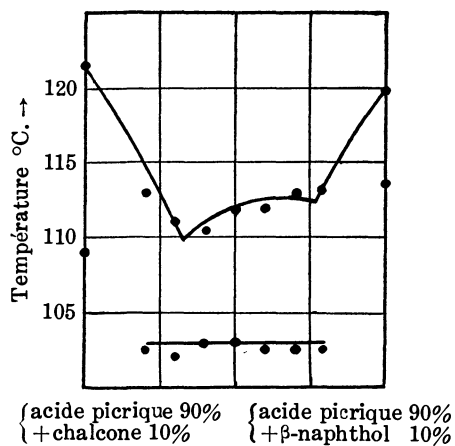


Fig. 13.

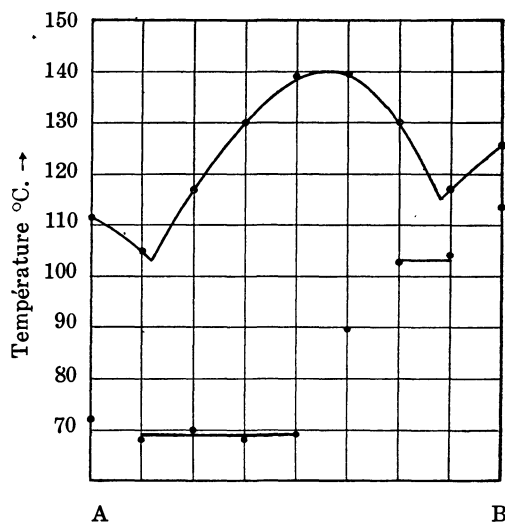


Fig. 14.

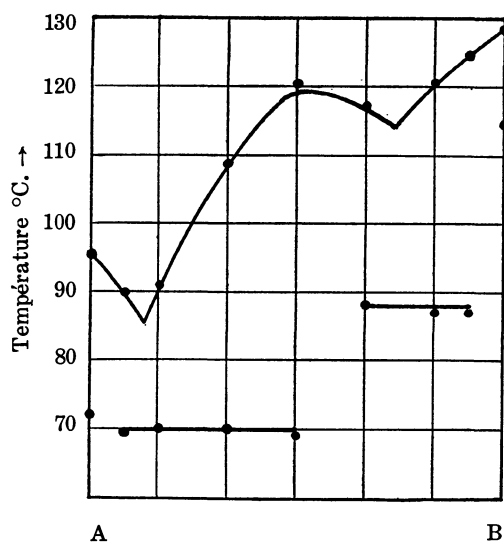


Fig. 15.

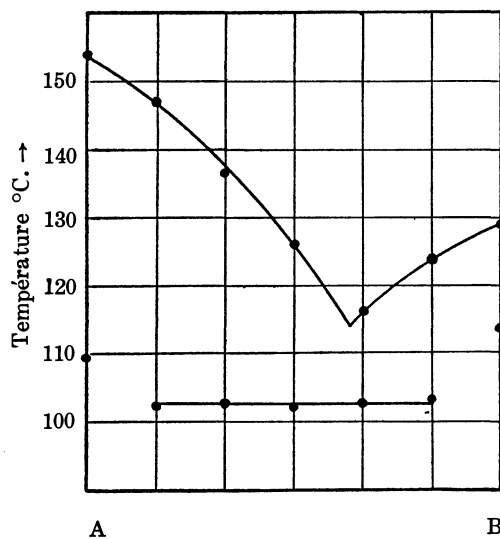


Fig. 16.

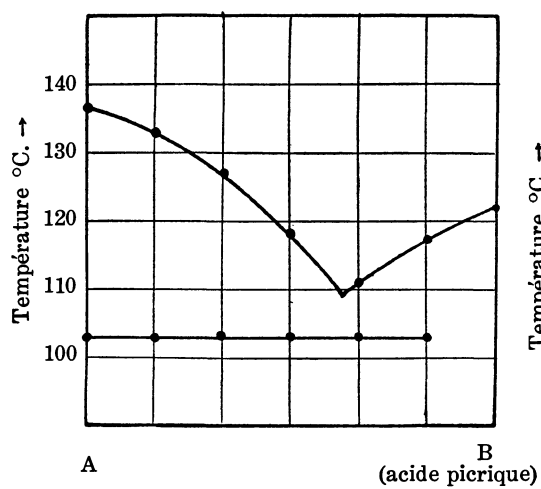


Fig. 17.

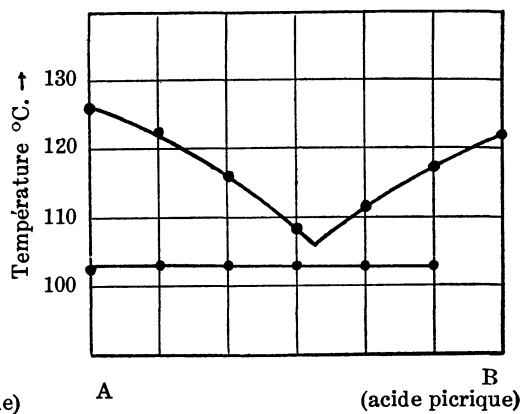
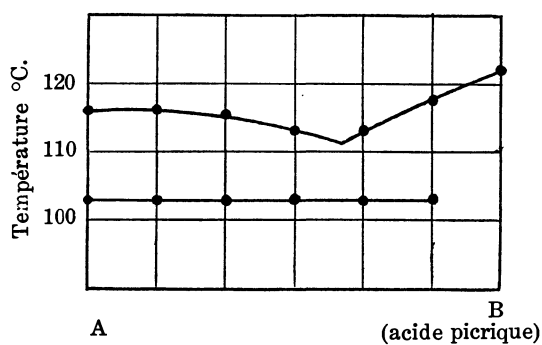
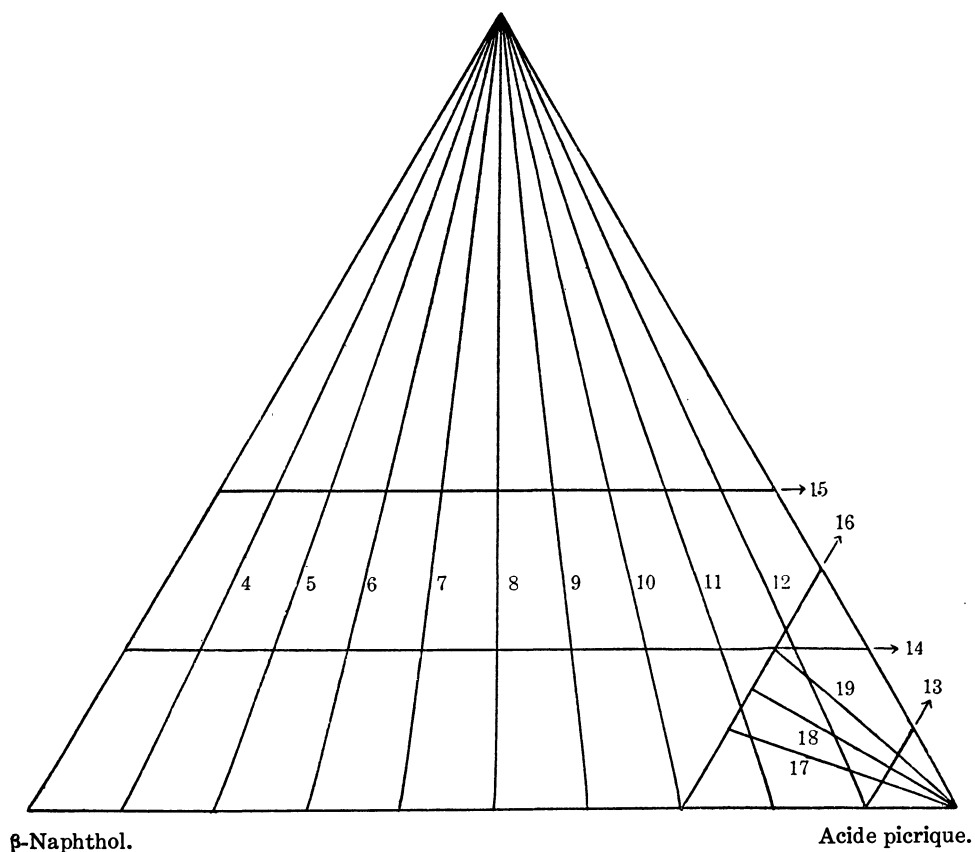


Fig. 18.



Méthylènedioxychalcone.



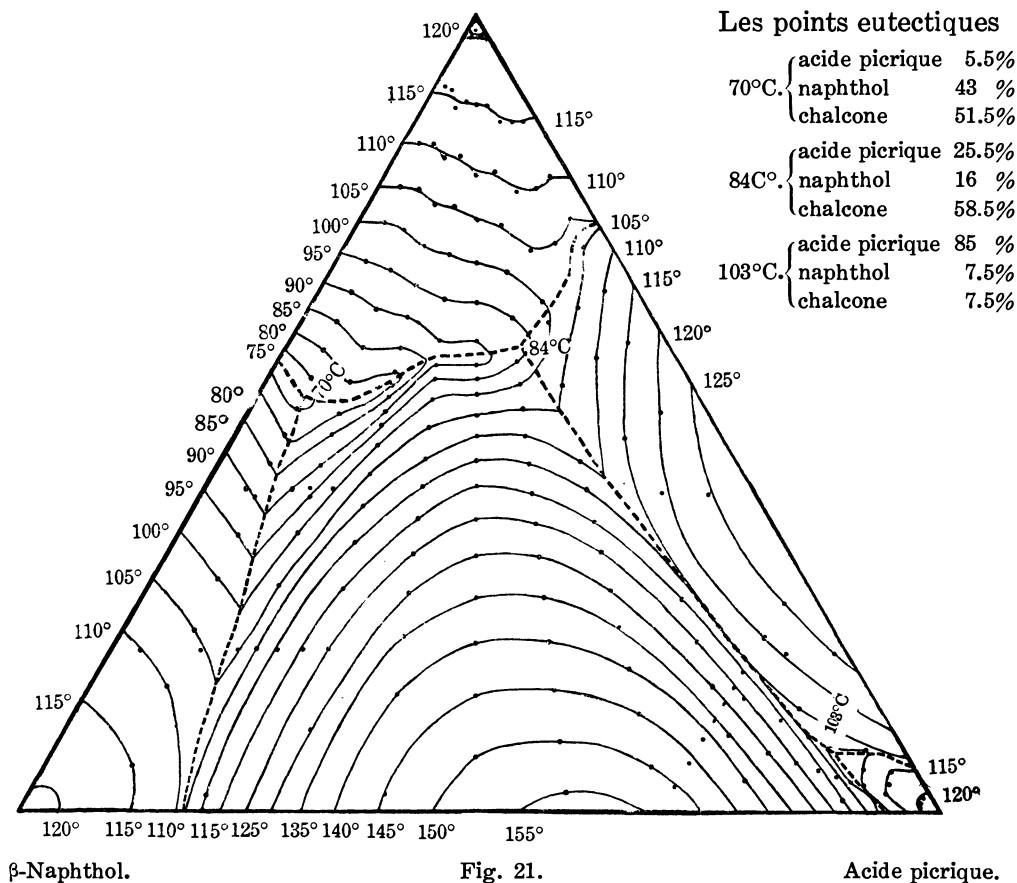
β-Naphthol.

Acide picrique.

Les chiffres sont identiques aux nombres des figures 4—19.

Fig. 20.

Méthylènedioxychalcone.



En terminant l'auteur tient à remercier a M. K. Yokoyama, aide privé, qui l'a assisté dans ses expériences et à M. le prof. Y. Shibata pour les conseils qu'il lui a prodigués.

Le Dr. Motte de la Maison franco-japonaise de Tokio, a eu la bonté de revoir ce mémoire au point de vue linguistique : nous l'en remercions sincèrement ici.

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RHYTHMIC PRECIPITATES. III. ON THE EFFECTS OF THE PRESENCE OF ACIDS, ALCOHOLS, OR AMINO-ACIDS IN GELATINE JELLIES.

By Toshizo ISEMURA.

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In the previous communication,⁽¹⁾ the author reported the effects on the rhythmic precipitates of light and the aging of gel before the superposition of the diffusing electrolyte on it. In the present paper the experimental results are described on the effects of the presence of some fatty acids, alcohols, and amino-acids in the gelatine jellies. It is a known fact that the addition of a small quantity of a capillarily active material such as fatty acids or alcohols decreases the surface tension of water, while the addition of some amino-acids increases it. It may be interesting, therefore, to study the effects of these substances on the bands of rhythmic precipitates.

Ordinary rhythmic precipitates of silver chromate in gelatine jelly have been tested. It is desirable, in the present experiment, that impurities contained in the gelatine should be as little as possible. Powdered "Gelatine white" from Merck has been dialyzed for about five days in distilled water. In this dialyzed gelatine the secondary rhythmic precipitates in gelatine-silver chromate system has no more been observed which were pointed out as the chloride and phosphate of silver.⁽²⁾

The gel was prepared by mixing equal volumes of the sol containing 0.2 per cent. potassium dichromate and the aqueous solution of the acid or alcohol. After 24 hours the 20 per cent. silver nitrate solution was superposed on the gel. Caution was taken so that in one series of experiments the sol used in preparing the jelly should be the same and the test-tubes should be of possibly equal diameters. Moreover, the heights of the jelly and the upper electrolyte in each test-tube were made as equal as possible.

The Effect of Fatty Acids. According to Traube's rule, the larger the molecular weight of the fatty acid in water is, the greater the decrease of surface tension of water is, provided the concentrations of the acid being the same. Propionic, butyric, capronic, and caprylic acids have been tested, and the gelatine jelly containing 0.05 mol. of the fatty acid per litre has been used. The results of the experiments are as follows:

(1) Isemura, this Bulletin, **8** (1933), 108.

(2) Hedge, "Liesegang Rings," (1932), 23. Riegel and Reihard, *J. Phys. Chem.*, **31** (1927), 713. Schleussner, *Kolloid-Z.*, **31** (1922), 347; **34** (1924), 338.

No acid : well-known rhythmic precipitates were observed.

Propionic acid : no band or a few faint bands were observed.

Butyric acid : no band or a few faint bands were observed.

Capronic acid : a few bands consisting of large crystals were observed.

Caprylic acid : two kinds of bands were recognized.

In the cases of propionic and butyric acids, bands did not appear in general. Under certain circumstances, however, a few bands have been observed near the contact surface with the upper electrolyte. In the case of capronic acid, several bands were observed, each of which was composed of considerably large crystals. This was caused, probably, by the deposition of silver chromate crystals on the initially formed bands of the silver soap. At first, white silver capronate in small granules deposits into bands, which then are coated gradually with brick-red silver chromate. The same process has been recognized much more distinctly in the case of caprylic acid. The solubility of caprylic acid in water is small, and the solution containing 0.05 mol. per litre is not homogeneous, but forms an emulsion. In this case, first the long orange layer of silver chromate deposited and in this layer the banding of comparatively large crystals were observed, which is considered silver caprylate. In the lower part of the test tube banding of white granules appeared, which then changed into brick-red in colour in the course of time. It is conceived that the granules of silver caprylate were coated with silver chromate.

In general, the addition of the fatty acid to the gel makes the particles of silver chromate larger. The greater the number of carbon atoms in fatty acid is, the more remarkable this effect is. From Traube's rule, it is known that the higher the fatty acid is in the homologous series, the greater depression is caused in the surface tension of the solution. It may be supposed that from the jelly of lower surface tension the deposition of crystals is easier than from the jelly of higher surface tension. By the addition of a fatty acid, therefore, the supersaturation limit of crystallization of silver chromate falls steeply, and this makes the banding impossible. But, on the contrary, the solubility of the silver salt of the fatty acid decreases with the increase in the number of carbon atoms in the acid. So the banding of silver soap occurs and that of silver chromate appears as a secondary phenomenon.

The Effect of Alcohols. The experiments on the effects of the addition of alcohols to the gel have been undertaken with methyl, ethyl, propyl, and butyl alcohols. The number of bands was examined in about 4 per cent. gelatine jellies containing 0.25 mol. of alcohol per litre. The concentrations of upper and lower electrolytes were the same as in the experiments with

acids. It was observed that the number of bands did not change on addition of the alcohol to the gelatine jelly. However, when the concentration of the alcohol in jellies was 0.5 mol. per litre the effect of the alcohol became distinct. The results are shown in Table 1.

Table 1.

Dispersion medium	Number of bands formed	
	alcohol 0.25 mol./l.	alcohol 0.5 mol./l.
no alcohol	19	19
with methyl alcohol	19	25
with ethyl alcohol	18	25
with propyl alcohol	19	26
with butyl alcohol	19	—

Table 2.

Conc. of methyl alcohol mol./l.	Number of bands formed
0	28
0.25	28
0.50	30
1.00	31
2.00	33

The effect of the concentration of methyl alcohol in the jelly on the number of bands is shown in Table 2.

Thus, the higher the concentration of the alcohol is, the greater the number of bands formed. It was observed that the distance between the upper surface of the jelly and the last-formed band was shorter in the jelly with higher concentration of the alcohol.

In short, the addition of the alcohol to the jellies makes the crystallization of silver chromate easier than without the alcohol. This may be caused, on one hand, by the depression of the surface tension of the jelly, and, on the other hand, by the depression of upper limit of supersaturation of silver chromate crystals, owing to the less solubility of gelatine in the aqueous solution of the alcohol, that means the less protective action of gelatine than in water. The number of bands, therefore, must increase on addition of the alcohol.

The Effect of Amino-Acids. The surface tension of the aqueous solutions of some amino-acids were measured by Ito.⁽¹⁾ He showed that glycine and alanine, unlike other amino-acids, increased the surface tension of water. So the effect on banding of silver chromate may be in the opposite direction to the case of the alcohol, that is to say the distance between bands will be wider and the number of the formed bands will be smaller.

(1) Ito, *Nippon Nogei-kwagaku-kaishi*, **6** (1930), 178, 930.

This was verified by the experiments. One of the results obtained is tabulated in Table 3.

Table 3.

Dispersion medium	Number of bands formed
without amino-acid	28
with 0.05 mol. glycine per litre	24
with 0.05 mol. alanine per litre	26

Glycine increases the surface tension more than alanine does, so the effect of the former is more remarkable than that of the latter.



The Formation of Rhythmic Precipitates of Silver Soap. It has been described in the preceding paragraph that the bands of silver capronate or silver caprylate accompanies the silver chromate bands. Moreover, the author succeeded in obtaining the rhythmic precipitates of silver soap only. Well dialyzed gelatine, freed from chlorides and phosphates, was dispersed into 4 per cent. sol, the acid was added, and then the whole was allowed to set. The concentration of the acid was between 0.05 and 0.1 mol. per litre. In the case of caprylic acid, an emulsion was formed. After setting the gel, 20 per cent. silver nitrate solution was poured on it. White thin bands appeared. The photograph shows an example of the bands of silver capronate. Thus two new examples of rhythmic precipitates were found, namely silver capronate and silver caprylate in gelatine jellies.

In conclusion the author expresses his hearty thanks to Prof. J. Same-shima of the Tokyo Imperial University for his kind advices.

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THE COLLOIDAL BEHAVIOUR OF SERICIN. II.*

By Hideo KANEKO.

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Sec. III. The Surface Tension of Sericin Sol.

H. Iscovesco⁽¹¹⁾ (1910) and Zlobicki observed that solutions of many hydrophilic colloids (egg white, ovoglobulin, starch, gum arabic) have a lower surface tension than pure water. The surface tension of normal blood serum is lower than that of pure water, and it is reasonable to assume that the decrease in surface tension of water is mostly caused by the proteins.

The experimental materials and the method are the same as described in the previous section.

(1) **Variation of Surface Tension with Temperature.** Fano and Mayer⁽¹²⁾ (1907) observed that the surface tension of the blood serum of any animal increases with fall in temperature, as is seen with water and with any other solution. I measured the surface tension of sericin sol with du Noüy's tensiometer at various temperatures. The results are shown in Table 15 and Fig. 9.

Table 15.

Surface tension (dyne/cm.) of
sericin sol (good "kaijo").

Temp. (C.)	0.48%	0.304%	0.228%	0.075%
0	59.00	61.00	61.50	63.70
10	56.89	58.91	58.80	62.00
20	54.22	56.50	57.10	60.32
30	52.33	53.81	55.75	58.01
40	49.49	51.00	53.61	55.50
50	46.78	48.50	51.40	54.33
60	44.45	45.95	49.57	51.65
70	43.02	44.25	48.96	50.36

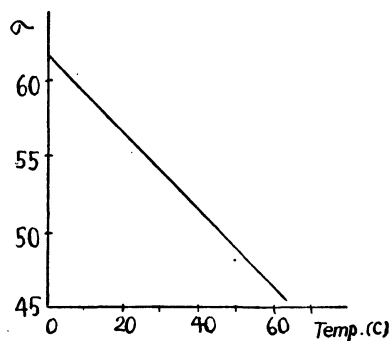


Fig. 9.

* Continued from p. 221 of this volume.

(11) H. Iscovesco, *Compt. rend. soc. biol.*, **69** (1910), 491, 537, 566, 622.

(12) Fano and Mayer, *Arch. fisiol.*, **4** (1907), 164.

Table 16.

	" Kaijo "		
	Good	Middle	Bad
Tan α	1.0575	0.7813	0.7346
Conc. (%)	0.304	0.346	0.309

The surface tension of sericin sol diminishes linearly with rise in temperature until about 60°C. . The value of $\frac{d\sigma}{dT}$ for sericin sol obtained from the cocoon of good " kaijo " is greater than that for sericin sol obtained from the cocoon of bad " kaijo. " Tangents of the angles of inclination of surface tension-temperature curves are shown in Table 16.

The relative lowering of surface tension is expressed by the term of $\frac{\sigma_0 - \sigma}{\sigma}$, where σ_0 and σ are respectively the surface tension of water and that of sericin sol. Some of results obtained are given in Table 17 and Fig. 10.

Table 17.

The values of $\Delta\sigma$.

Temp. (C.)	Good (0.304%)	Mid. (0.347%)	Bad (0.309%)
0	0.2344	0.3005	0.3095
10	0.2553	0.3221	0.3271
20	0.2849	0.3417	0.3419
40	0.3715	0.3941	0.4032
60	0.4646	0.4513	0.4608
70	0.4915	0.4735	0.4687

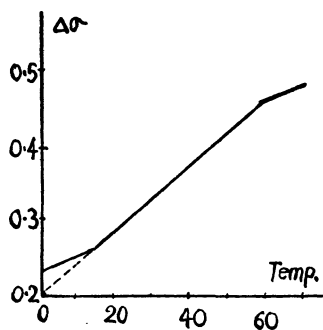


Fig. 10.

It can be seen that the curve is in three branches. This is due to the fact that below 18°C. sericin exists as gel form, above 60°C. as sol form, and between these temperatures as a mixture of two forms. This result is coincident with that obtained in the change of viscosity with temperature.

If the free energy expressed by Gibbs-Helmholz' equation, F , is substituted by the surface tension, free energy per unit area, the following equation results :

$$U_s = \sigma - T \frac{d\sigma}{dT} .$$

$T \frac{d\sigma}{dT}$ is the heat energy which is necessary to form unit area at constant temperature.

Differentiating the above equation :

60°C.

Time (min.)	Good (0.323%)	Mid. (0.310%)	Bad (0.300%)
10	44.75	44.05	45.70
30	44.34	43.73	45.46
60	43.51	43.35	45.41
120	43.45	43.05	44.95
180	43.38	42.92	44.70

At 40°C., where the greatest variation of $\frac{\Delta\sigma}{\Delta T}$ occurs, the variation of surface tension with time is also the greatest as shown in Table 19.

(3) **Variation of Surface Tension with Concentration.** Bottazi⁽¹⁴⁾ (1911) drew the general conclusion that proteins in a state of perfect solution lower the surface tension of water,

and that the reduction is, to a certain extent, proportional to their concentrations. From my experimental results it can be seen that the surface tension of sericin solution diminishes with increasing concentration and that it has the following relation with concentration :

$$0.1\sigma + \log 100.c = \text{constant} = k,$$

where σ is the surface tension of sericin sol and c is its concentration in gram per 100 c.c.. The results are summarized in Table 20 and plotted in Fig. 12. The value of constant K is about 6.7 and it varies slightly with "kaijo" of cocoons.

(4) **Effect of Salts, Acids, and Alkalis on the Surface Tension.** (a) **Salts.** By a series of investigations on gelatin solutions, W. Frei⁽¹⁵⁾ (1908) found that the anions, SO_4'' , Cl' , and NO_3' , raise the surface tension of neutral gelatin in the order given, while the cations, Na' , K' , and Mg'' , raise it about in the same order as they increase the surface tension of water, and that the anions raise it in the order NO_3' , SO_4'' , and Cl' , if the solution is acid. The surface tension of neutral solutions is raised

Table 20.
Surface tension (dyne/cm.) of sericin sol (good "kaijo.")

Temp. \ Conc. %	0.383	0.256	0.191	0.127	0.096	0.048	0.024	0.012
20	53.39	54.53	55.56	57.21	58.33	60.62	62.95	65.95
30	51.20	52.47	53.23	55.06	56.26	60.01	61.98	65.06
40	48.86	50.01	51.20	52.61	54.15	58.16	60.23	64.11
50	47.05	48.62	49.25	51.18	52.83	57.03	58.31	62.08
60	45.58	46.00	46.93	49.01	50.78	55.42	57.00	60.55

(14) Bottazzi, "Viscosity and surface tension of suspensions and solutions of muscle proteins under the influence of acid and alkali."

(15) W. Frei, "Physical chemistry and veterinary science."

"Kaijo"	Const. K (20°C.)
Good	6.792
Middle	6.783
Bad	6.678

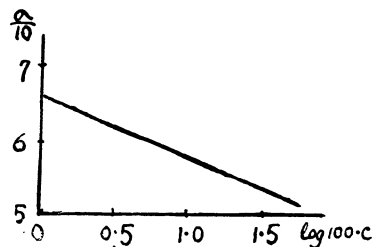


Fig. 12.

by OH-ions and lowered by H-ions. The surface tension of protein solutions may be raised by the addition of electrolytes which can increase the degree of dispersion of the protein.

The results obtained are collected in Table 21.

Table 21. Influence of salt solutions (0.1 N).

V c.c.	NaCl	NaNO ₃	NH ₄ Cl	CaCl ₂	FeCl ₃	Th(NO ₃) ₄
	0.15%	0.083%	0.083%	0.106%	0.07%	0.07%
0.0	55.26	57.83	57.23	58.91	57.00	57.00
0.05	55.89	—	—	58.24	57.52	61.32
0.1	56.21	58.12	57.00	58.12	57.56	62.63
0.2	55.83	58.44	56.91	57.61	60.62	63.20
0.3	55.64	58.73	56.85	57.21	61.83	62.68
0.5	55.58	58.88	56.34	57.42	60.60	62.30
0.7	55.70	58.06	55.65	57.17	60.63	62.35
1.0	55.76	58.00	55.21	56.65	60.36	62.32

(1) When an electrolyte like NaCl, NaNO₃, KI, KNO₃, NH₄SCN, MgCl₂, FeCl₃ or Th(NO₃)₄, is added to a sericin solution the surface tension rises to a maximum and then diminishes. (2) In the cases of NH₄Cl, CaCl₂, CaSO₄, Ca(NO₃)₂, or Ca₃(PO₄)₂ the surface tension goes on decreasing if the amount of the electrolyte is increased. (3) The surface tension increases with increasing concentration of an electrolyte like Na₂CO₃, Na₂SiO₃, etc.. The electrolytes belonging to the first class give also a maximum or a minimum point to the electrokinetic potential of sericin sol

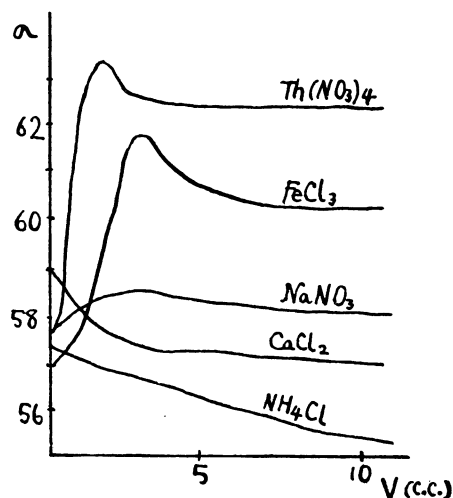


Fig. 13.

as shown later. The surface tension, therefore, have an intimate relation with the electrokinetic phenomena.

If σ_m be the maximum lowering value of the surface tension of sericin sol containing a salt and σ_0 the surface tension of it with no salt, the difference of these two values, $\sigma_0 - \sigma_m$, is shown in the Table 22.

The sericin solution obtained from cocoons of good "kaijo" is more affected by the monovalent cations and less by the polyvalent cations than that obtained from cocoon of bad "kaijo." By a series of investigations with sericin solutions, I found that the cations, Na^+ , Mg^{++} , and Fe^{+++} , raise the surface tension of sericin in the order given at low concentrations.

Table 22.

"Kaijo"	NaNO_3	FeCl_3	$\text{Th}(\text{NO}_3)_4$
	$\frac{\sigma_0 - \sigma_m}{C}$	$\frac{\sigma_0 - \sigma_m}{C}$	$\frac{\sigma_0 - \sigma_m}{C}$
Good	18.07	69.0	88.6
Middle	14.00	76.9	108.2
Bad	3.60	82.4	103.8

(b) **Acids and alkalis.** W. Frei noticed that the surface tension of neutral gelatin solutions is raised by small amounts of hydroxyl-ions and depressed by hydrogen-ions. The values of the surface tension of sericin sol at various pH values effected by addition of various amounts of 0.1 N hydrochloric acid given in Table 23.

Table 23. (at 20°C.)

Good (0.092%)		Mid. (0.072%)		Bad (0.081%)	
pH	σ	pH	σ	pH	σ
6.07	56.70	6.36	59.20	6.53	57.41
5.21	54.20	5.40	57.21	5.46	55.12
4.69	52.96	4.63	55.96	4.90	54.33
4.00	53.08	4.11	55.70	4.30	54.08
3.75	53.30	3.75	56.10	3.80	54.62
3.54	54.45	3.25	57.86	3.46	55.38
3.32	55.05	3.17	59.11	3.28	55.75
3.25	56.51	3.05	60.38	—	—

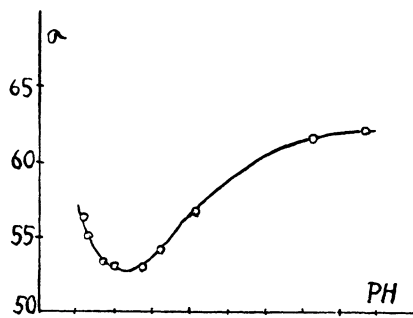


Fig. 14.

Fig. 14 shows that the addition of the acid first lowers the surface tension, and then increases it, and that the addition of the alkali gradually raises the surface tension.

The maximum lowering of the surface tension of the sericin solution corresponds to the isoelectric point of the dissolved sericin, because molecules are more efficacious than ions in lowering the surface tension of water. So we can determine the isoelectric point of a soluble protein by measuring the surface tension of its solution.

Table 24.

" Kaijo "	Isoelec. point (maximum lowering point)	Conc. (%)
Good	pH 4.25	0.092
Middle	4.30	0.072
Bad	4.40	0.081

The isoelectric point of the sericin solution obtained from cocoons of good " kaijo " exists at a more acid side than that of the sericin solution obtained from cocoons of bad " kaijo " (Table 24). It depends, therefore, upon the " kaijo " of cocoons and also upon the concentration of the sericin solution.

The effect of sulphuric acid on the surface tension of the sericin solution is similar to that of hydrochloric acid, but the former shows the slower change of the surface tension with pH values than the latter. For the organic acids, succinic, tartaric, and citric acids, the degree of the lowering of the surface tension, $\Delta\sigma$, is given in Table 25.

Table 25.

" Kaijo "	Tartaric acid $\Delta\sigma = \frac{\sigma_0 - \sigma_m}{C}$	Succinic acid $\Delta\sigma$	Citric acid $\Delta\sigma$
Good	72.2	88.2	87.8
Middle	89.1	126.5	112.4
Bad	104.3	143.3	133.2

The effects of these acids are remarkable in the case of the sericin solution obtained from cocoons of bad " kaijo. " The effects of fatty acids on the surface tension of sericin sol obtained from outer layer of cocoons are shown in Table 26 and Fig. 15.

Table 26. (Conc. = 0.07%).

Vol. of acid added in c.c.	Formic acid (dyne/cm.)	Acetic acid (dyne/cm.)	Butyric acid (dyne/cm.)
0.	56.17	56.17	56.17
0.1	56.05	55.42	53.69
0.2	55.82	54.84	45.59
0.3	55.50	54.26	48.42
0.5	55.15	52.65	46.00
0.7	54.97	51.92	43.37
1.0	54.26	50.76	42.05

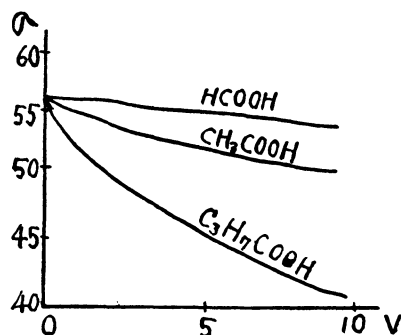


Fig. 15.

I. Traube⁽¹⁶⁾ showed that capillary-active organic substances lower the surface tension to an increasing degree as the length of the carbon chain increases in the homologous series. This regular change in the surface tension can be seen in Table 26.

On the addition of alkali like 0.1 *N* NH₄OH, NaOH, etc., the surface tension of the sericin solution increases to a maximum at a certain alkali concentration as shown in Table 27.

Table 27.

Variation of surface tension with alkali concentration.

Vol. of alkali added in c.c.	0.1 <i>N</i> NH ₄ OH		0.1 <i>N</i> NaOH	
	$\sigma \left(\frac{\text{dyne}}{\text{cm.}} \right)$	pH	σ	pH
0.0	56.70	6.07	56.70	6.07
0.05	58.63	7.39	61.55	9.29
0.1	58.81	8.72	62.01	10.59
0.2	59.70	10.21	61.86	—
0.3	59.05	—	61.63	—

At the isoelectric point the sericin solution becomes most turbid and upon the addition of sodium hydroxide the dispersed phase passes gradually into a state of solution and at the same time the solution turns to yellow.

Sec. IV. The Probable Dimension of the Sericin Particle on the Surface of the Sericin Solution.

P. L. du Noüy⁽¹⁷⁾ (1925) presumed that the time drop of the surface tension of a solution was due to the variation in arrangement of dispersed particles on the surface and he calculated the probable dimension of molecules from the relation between the maximum position of time drop of the surface tension and the space property of protein molecules. He considers that in high concentrations the protein molecules aggregate irregularly on the surface of the solution and exert only a part of their polar groups to lower the surface tension and at low concentrations they have a free space (gap) between them and move freely through the surface. When the protein molecules closely contact with together at an adequate concentration, the time drop of the surface tension will be strong. By this con-

(16) I. Traube, *Ber.*, **17** (1884), 2294; *J. prakt. Chem.*, **34** (1886), 292.

(17) P. L. du Noüy, *J. Biol. Chem.*, **64** (1925), 595-613.

sideration he found that egg albumin formed a monomolecular film on the surface of the solution. F. Hervik (1931)⁽¹⁸⁾ also showed that serum albumin existed in a similar condition.

Two c.c. of sericin solution of various concentrations were poured into watch-glasses of the same radius of curvature and the surface tensions were measured with du Noüy's tensiometer immediately and after two hours at room temperature. In Table 28 $\Delta\alpha$ expresses the difference of the rotation angle of the tensiometer.

Table 28. Good "kaijo."

Conc. (%)	Time drop (2 hours later) $\Delta\sigma$	Conc. (%)	Time drop (2 hours later) $\Delta\alpha$
0.52	-0.4	0.392	0.3
0.052	0.1	0.0392	0.0
0.0052	4.3	0.00392	5.8
0.00104	6.0	0.000784	6.1
0.00052	4.3	0.000392	4.0
0.000052	3.0	0.0000392	0.1
0.0000052	1.1	0.00000392	2.7

The concentration of sericin corresponding to the maximum time drop of surface tension are shown in Table 29.

Table 29.

Original conc. (%)	Conc. at max. drop. (%)	Quantity of sericin in 2 c.c. (g.)
0.52	0.00104	2.08×10^{-5}
0.392	0.001306	2.612 "
0.34	0.001133	2.266 "
0.22	0.00110	2.20 "
0.214	0.00107	2.14 "

Table 30.

Original conc. (%)	Width of surface layer (A. U.)
0.52	53.8
0.392	58.5
0.34	59.5
0.22	56.4
0.214	57.9

If the sericin particles aggregate throughout on the surface (between air and the solution, and between solution and the glass surface), the quantity of sericin must be equal to $\frac{G}{S}$ in cm., where G is the weight of sericin contained in the surface and S is the total area of the surface of the solution and equals to 26.53 sq. cm. in this case. The probable dimension of sericin particles therefore, is $\frac{G}{S} \cdot \frac{1}{d}$, where d is the specific gravity of sericin.

(18) F. Hervik, *Kolloid-Z.*, **56** (1931), 1-7.

The width of sericin layer calculated from the above assumption are shown in Table 30.

The probable dimension of the sericin layer on the surface of the sericin solution corresponds in average to 57.2 A. U. for sericin obtained from cocoons of good "kaijo."

Sec. V. The Dispersity of Sericin Particles in the Aqueous Solution.

The sericin solution is a poly-dispersed system of sericin particles, so the rates of diffusion may vary within wide limits. The sericin solutions obtained from cocoons of various "kaijo" are different in viscosity, coagulation by electrolytes, or Tyndall's phenomena. This may be partly due to the difference in size of sericin particles.

In 1929 J. H. Northrop and M. L. Anson⁽¹⁹⁾ gave a method for the determination of diffusion constants in the case of substances which cannot be obtained in a pure solution. The diffusion constant, D , is defined as the quantity of material that diffuses across a plane of unit dimensions in unit time under unit concentration gradient. The speed of diffusion is governed by the law of Fick, which is expressed in the equation:

$$dQ = DS \frac{dc}{dx} dt \quad \text{or} \quad D = \frac{dQ}{S dt \frac{dc}{dx}},$$

where dQ is the quantity which passes across the plane of area S in time dt under a concentration gradient of $\frac{dc}{dx}$. The solute diffuses from concentration C to concentration zero (pure solution) and if the volume of these solutions is relatively large and the experiment is carried on for a short time, the concentration may remain practically constant. Let the effective area of the pores be S , the effective length be l and the quantity diffusing in time t be Q , then above equation becomes simply

$$D = \frac{Q}{S t \frac{c}{l}} = \frac{l}{S} \cdot \frac{Q}{t c} = K \frac{Q (\text{sq. cm.})}{t (\text{day})},$$

where Q is the number of c.c. of the concentrated solution that contains the amount of the substance diffused, and K is l/S . In order to obtain the value of constant K it is necessary to standardize the apparatus with hydrochloric acid solution the diffusion coefficient of which is known.

(19) J. H. Northrop and M. L. Anson, *J. General Physiol.*, **12** (1929), 543.

$$K = \frac{D t}{Q}$$

After this constant has been determined for a definite membrane it may be used to determine the diffusion coefficient of sericin particles.

The apparatus was similar to that used by Northrop and Anson except that the diffusion membrane used was hard filter paper (Carl Schleicher and Schüll, No. 597). The cell contained 17 c.c. and the outside liquid, pure water, was 50 c.c.. The cell was filled with the sericin solution and rinsed with water. The diffusion was allowed to continue until the desired amount has passed through the membrane at 18°C..

The amount of sericin diffused into the outside liquid in a definite time was determined by Kjeldahl's method.

Exp. 1 Q (equivalent c.c.)				Exp. 2 Q			
$t = 15$ hours	No. 1	2.85	mean	No. 1	2.90	mean	
	No. 2	2.97		No. 2	2.83		
	No. 3	2.79		No. 3	29.4		
			2.87			2.89	

Total average = 2.88 c.c.

Therefore, the diffusion coefficient is

$$D = K \frac{Q}{t} = 0.02873 \times \frac{2.88}{\frac{15}{24}} = 0.1240 \frac{\text{sq. cm.}}{\text{day}}.$$

According to Einstein the diffusion coefficient is related to the radius of the molecule, r , by the following equation:

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi r \eta},$$

where R is the gas constant in erg/deg. mole, N Avogadro's constant, η the viscosity of water at 18°C., and T absolute temperature.

$$r = \frac{RT}{N} \cdot \frac{1}{6\pi D \eta} = 1.430 \text{ m}\mu. \text{ for } 0.198\% \text{ solution.}$$

The molecular weight of the sericin particle may be calculated from the radius r by the following equation provided the specific gravity, S , is known:

$$M = \frac{4}{3} \pi r^3 SN \text{ (if the particle be spherical),}$$

$$M = 10618.91 \text{ for } 0.198\% \text{ solution } (S = 1.43).$$

From this results I can presume that readily diffusible sericin particles are molecular colloids.

By the optical method H. R. Bruins⁽²⁰⁾ showed that the hydrophilic colloids like starch, gum arabic, etc. have an anomalously large diffusion velocity and that the radius is nearly equal to that of a molecularly dispersed substance. The relations between the concentration of the sericin solution and the diffusion coefficient thus calculated are shown in Table 31.

Table 31.

Conc. (%)	Time (hours)	Volume (c.c.) of sericin diffused	D (sq. cm./day)	$r \times 10^7$ cm.	M
0.388	16	2.05	0.0882	2.009	29440.57
0.294	16	2.58	0.1110	1.596	14774.19
0.266	16	2.85	0.1228	1.444	10922.41
0.198	15	2.83	0.1239	1.430	10618.91
0.142	15	3.05	0.1400	1.266	7366.62

In low concentrations the size of sericin particles increases with increasing concentration and above 0.5 per cent. the rate of increase becomes very small. In the case of the same concentration sericin particles obtained from cocoons of good "kaijo" are larger than those obtained from cocoons of bad "kaijo."

Table 32.

Conc. (%)	$\ln r$	$\frac{\ln r}{C} = A$
0.388	0.6973	1.796
0.294	0.4653	1.566
0.266	0.3678	1.381
0.198	0.3572	1.803
0.142	0.2355	1.658

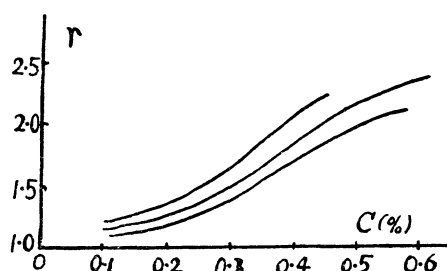


Fig. 16.

The logarithm of the radius of sericin particles is approximately proportional to the concentration. (Table 32 and Fig. 16.)

(20) H. R. Bruins, *Kolloid-Z.*, **54** (1931), 265; *ibid.* **57** (1931), 152.

As shown later the radius of sericin particles is proportional to the specific conductivity k in low concentration (Table 33.)

Table 33.

Conc. (%)	$r(\text{m}\mu.)$	Sp. cond. $k \times 10^3$	$\frac{k \times 10^3}{r}$
0.636	2.372	0.636	0.268
0.40	1.786	0.530	0.296(?)
0.266	1.423	0.368	0.259
0.25	1.401	0.350	0.250
0.22	1.351	0.330	0.244
0.15	1.189	0.299	0.251
0.132	1.189	0.298	0.250

The calculated weight of micellæ in similarly prepared solutions varies with the concentration and with "kaijo" of the cocoon. Thus in a 0.3 per cent. solution the mean micellar weight is about 15000 for sericin obtained from cocoon of good "kaijo."

Effect of Acid and Alkali. It is

well known that the micellar size of protein particles varies with the pH value of the solution. Then, the diffusion coefficient of sericin must decrease on addition of small amounts of acid and increase on addition of alkali. The experimental results are given in Table 34.

Table 34. $C = 0.388\%$ (good "kaijo," 18°C.)

	pH	D	$r(\text{m}\mu.)$	M
Original solution	5.53	0.0882	2.009	29440.58
+ 0.01 N HCl	4.88	0.0796	2.226	40061.38
+ 0.01 N NaOH	6.02	0.0903	1.963	27453.60

Table 35.

Relative viscosity η	Refractive index n (18°C.)	$\frac{n}{\eta}$
1.147	1.34828	1.17
1.141	1.34812	1.18
1.136	1.34802	1.18
1.129	1.34796	1.19
1.121	1.34784	1.20
1.109	1.34773	1.21

Sec. VI. The Optical Properties of the Sericin Solution.

(1) **The Refractive Index of the Sericin Solution.** D. von Dusœe⁽²¹⁾ measured optically the concentration of proteins as the function of refractive index. I found that in low concentrations the refractive index of the sericin solution is proportional to its viscosity, and depends on the concentration, hydration, the form and size of sericin particles, etc.. And at the same concentration the refractive index of sericin sol obtained from the cocoons of good "kaijo" is greater than that of sericin sol

(21) D. von Dusœe, *Biochem. Z.*, **230** (1931), 373, 383; **244** (1932), 382.

obtained from the cocoons of bad "kaijo." The relation between the relative viscosity and the refractive index is shown in Table 35.

(2) **The Optical Activity of the Sericin Solution.** Sericin solutions are lævorotatory. Vignon⁽²²⁾ observed that both sericin and fibroin, two constituents of silk, were lævogyrate and their rotatory powers were about equal and approximately -35° .

Sericin	$[\alpha]_D$
From Japanese cocoons	-31.3
From Chinese cocoons	-33.9
From Tonking cocoons	-43.6

These value were obtained with the solution of sericin in 3 per cent. NaOH, but in such a strongly alkaline solution the optical activity of sericin may be reduced as is the case with gelatin. In researches made by

T. Watanabe⁽²³⁾ it was observed that the specific rotation of sericin dissolved in 0.3 per cent. NaOH solution is on an average about -80° . I measured the rotatory power of the sericin solution with Landolt's polarimeter under the light of the sodium flame and the experimental materials were the following:

Variety of cocoons	" Kaijo "
" Nichi " No. 1 $\times$ " Shi " No. 4 (1930)	good
" Nichi " No. 107 $\times$ " Shi " No. 101 (1930)	middle
" Nichi " No. 110 $\times$ " Shi " No. 103 (1930)	bad

(a) **Variation of Optical Activity with Concentration.** The specific rotation of sericin is not constant, but it varies with concentration (Table 36). This may be due to the variation of aggregation of sericin micellæ.

Table 36.

Good " kaijo "		Mid. " kaijo "		" Bad kaijo "	
Conc. (%)	$[\alpha]_D$	Conc. (%)	$[\alpha]_D$	Conc. (%)	$[\alpha]_D$
0.14	-118.10	0.12	-123.15	0.13	-124.22
0.16	-110.55	0.15	-111.00	0.16	-105.83
0.18	-105.23	0.18	-103.56	0.18	- 96.33
0.20	-102.20	0.20	-100.10	0.20	- 88.40
0.22	- 95.82	0.24	- 90.67	0.24	- 78.04
0.26	- 93.50	0.28	- 83.16	0.26	- 74.38
0.29	- 91.72	0.30	- 80.00	0.31	- 70.49
0.33	- 89.10	0.35	- 79.05	0.34	- 64.11
0.35	- 88.71	0.40	- 78.62	0.40	- 62.40
0.40	- 86.25	0.42	- 78.19	—	—

(22) Vignon, *Compt. rend.*, **103**, 802.

(23) T. Watanabe, *J. Sakurakai, Japan*, December, 1929.

As shown in Table 36, the specific rotation of sericin is lævorotatory and diminishes with increasing concentration. The sericin solution obtained from the cocoon of good "kaijo" shows greater specific rotation than that obtained from the cocoon of bad "kaijo" at the same concentration.

The optical activity of the sericin solution dialyzed for 15 hours in running water is approximately equal to that of the sericin solution not dialyzed.

Table 37.

Good (0.21%)		Mid. (0.22%)		Bad (0.13%)	
pH	$[\alpha]$	pH	$[\alpha]$	pH	$[\alpha]$
5.83	98.71	5.75	94.93	5.35	120.00
5.13	94.62	5.33	96.40	4.81	116.17
4.50	69.05	4.50	75.45	4.30	103.00
4.24	52.24	4.50	55.00	4.14	97.70
4.05	61.12	4.05	55.50	4.00	110.15
3.95	73.10	3.87	83.81	3.93	116.17
3.46	101.50	3.62	93.30	3.50	124.41
3.11	101.68	3.11	106.81	3.06	126.53

Table 38.

Vol. added c.c.	Good (0.18%)	Mid. (0.15%)	Bad (0.11%)
0	105.78	113.73	125.89
0.05	125.22	128.93	152.64
0.1	141.67	154.80	171.18
0.3	100.83	133.60	146.64
0.5	122.78	129.61	137.89
0.7	132.22	162.23	—

(b) **Effect of Acid and Alkali on Optical Activity.** Under the influence of hydrogen-ions the rotation of sericin decreases and it shows a minimum value at the isoelectric point of sericin.

(i) **Hydrochloric acid (0.01 N).** In the 0.2 per cent. sericin solution the isoelectric point corresponds approximately to pH 4.20. With sulphuric acid and oxalic acid the same phenomena can be seen.

(ii) **Sodium hydroxide (0.1%).** It can be seen that on addition of alkali to the sericin solution the rotatory power increases to a maximum and then diminishes. The maximum value corresponds nearly to the neutral point of the solution. The effect of alkali on the optical activity of sericin is the greatest for the sericin solution obtained from the cocoon of good "kaijo" (Table 38).

(c) **Effect of Salts on the Optical Activity.** The asymmetry of the sericin micellæ may vary with concentration, with different "kaijo" of the cocoon, and on addition of electrolytes. The rotation of sericin increases if the hydration is raised, for example, by the addition of alkali or salts with a pronounced lyotropic action.

Table 39.

Volume added in c.c.	(NH ₄) ₂ CO ₃	CH ₃ CO ₂ Na	Na ₂ CO ₃	Na ₃ PO ₄	NaCl	C ₄ H ₄ O ₆ K.Na
	(0.26 %)	(0.3%)	(0.32%)	(0.2%)	(0.21%)	(0.18%)
0	93.54	90.67	89.81	105.00	98.43	105.33
0.05	100.33	135.80	99.81	97.71	85.09	140.67
0.1	134.38	108.49	83.56	90.53	101.76	140.11
0.3	103.54	126.80	111.56	127.13	110.00	134.59
0.5	88.54	151.00	98.52	134.50	100.61	—
0.7	70.33	126.11	91.50	125.46	—	—

(Conc. of salt solutions is 0.1 per cent.)

The specific rotation of the solution attains a maximum on increasing the amount of the salt, the effect of Rochelle salt being the strongest (Table 39). Potassium bitartrate, glycocoll, etc. affect also strongly the rotation.

Sec. VII. The Electric Conductivity of the Sericin Solution.

Proteins differ from ordinary electrolytes in having a large cumbersome ion which may arise from several aggregated molecules. According to the investigation by Whitney and Blake (1904) the specific conductivity k is 68×10^{-6} mho for 0.2 per cent. gelatin sol. Although the protein solution is purified by dialysis, the state of aggregation of sericin micellæ changes at the same time and the variation of its electric conductivity may be caused by this treatment. For this reason, I employed the non-dialyzed sericin solution for measurement of its electric conductivity. The electric conductivity was measured by Kohlrausch's method and the cell constant was 0.1578.

(1) Variation of Specific Electric Conductivity with Concentration. The experimental results are shown in Table 40 and in Fig. 17.

Table 40.

Good "kaijo"		Middle "kaijo"		Bad "kaijo"	
Conc. C (%)	Sp. cond. $k \times 10^3$	Conc. C (%)	Sp. cond. $k \times 10^3$	Conc. C (%)	Sp. cond. $k \times 10^3$
0.800	0.6326	0.771	0.6481	0.861	0.6502
0.588	0.6070	0.625	0.6362	0.680	0.6452
0.578	0.5955	0.548	0.6340	0.580	0.6341
0.508	0.5718	0.538	0.6173	0.532	0.6251
0.480	0.5636	0.480	0.6014	0.470	0.6056
0.427	0.5091	0.430	0.5641	0.390	0.5537
0.412	0.4931	0.380	0.5349	0.374	0.5232
0.370	0.4265	0.360	0.4849	0.335	0.4622
0.300	0.3981	0.320	0.4157	0.265	0.3945
0.270	0.3431	0.281	0.3857	0.250	0.3670
0.234	0.3260	0.170	0.3051	0.194	0.3076
0.160	0.3086	0.104	0.2982	0.140	0.3006
0.000	0.3564	0.000	0.3564	0.000	0.3564

The sericin solutions prepared by boiling the cocoon layer with water contain a very small amount of electrolytes as impurities and combined form, so the specific electric conductivity has a remarkably high value. The degree of aggregation of sericin micellæ and the amount of electrolytes present in it may vary with increasing concentration, so the electric conductivity will increase with increasing concentration. But, the rate of

variation, $\frac{dk}{dc}$ is the greatest near the concentration of 0.35 per cent. The specific electric conductivity k of the sericin solution is a linear function of the logarithm of the concentration, C , as shown in the following formula:

$$k = \log 100.C + B,$$

where B is constant but varies with "kaijo" of the cocoon. The value of constant B for the sericin solution obtained from the cocoon of good "kaijo" is larger than that for the sericin solution obtained from the cocoon of bad "kaijo."

"Kaijo"	Const. B
Good	1.117
Middle	1.096
Bad	1.077

I already found the same relation in the case of surface tension of the sericin solution.

(2) **Variation of Electric Conductivity with Temperature.** The colloidal state and adsorption capacity of sericin micellæ are affected by the variation of temperature. On raising temperature sericin particles transform gradually from gel state into sol state and the adsorption capacity diminishes. So the electric conductivity of the sericin colloid increases with rise in temperature (Table 41).

Table 41. Sp. elec. conductivity at various temperatures.

0°C.		20°C.		40°C.	
C (%)	$k \times 10^3$	C (%)	$k \times 10^3$	C (%)	$k \times 10^3$
1.154	0.4971	1.100	0.6210	1.154	1.1435
0.718	0.5058	0.771	0.6481	0.718	1.0944
0.580	0.4439	0.548	0.6340	0.500	0.8125
0.386	0.3507	0.380	0.5349	0.364	0.5844
0.200	0.2700	0.281	0.3857	0.200	0.4331

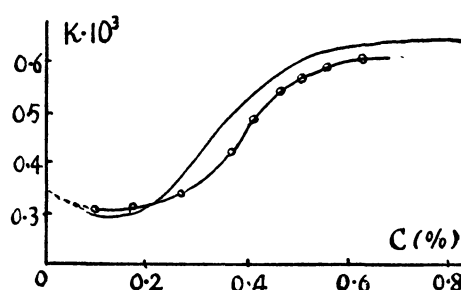


Fig. 17.

When potassium chloride is added to the sericin solution, the electric conductivity has a maximum and then diminishes with increasing concentration of the salt and the effect of the salt is the greatest for bad "kaijo."

(3) **Variation of Electric Conductivity with Time.** The specific electric conductivity of the sericin solution varies irregularly with time and diminishes during about two hours and then gradually increases. The minimum point corresponds approximately to a maximum point of viscosity varying with time (Table 42).

Table 42. The variation of k with time.

Time (min.)	Good (0.530%) $k \times 10^3$	Mid. (0.562%) $k \times 10^3$	Bad (0.390%) $k \times 10^3$
0	0.5802	0.6321	0.5516
15	0.5883	0.6363	0.5537
30	0.6069	0.6641	0.5845
45	0.5845	0.6117	0.5396
60	0.5636	0.5845	0.5095
75	0.5442	0.5856	0.4931
90	0.5260	0.5537	0.4856
105	0.5091	0.5296	0.4891
120	0.4931	0.5296	0.5179
150	0.5349	0.5380	0.5759
180	0.5618	0.5537	0.6117

The conductivity increases under the same condition as the number of ions. This variation may be due to the change of the number of ions and also of surface property of sericin micellæ.

(4) **Effect of Acid and Alkali on Electric Conductivity.** It is probable that the conductivity of the protein is due mostly to combined or adsorbed salts. If a strong acid be gradually added to a sericin solution, the volume of the solution being kept constant, and the electric conductivity be determined after each addition, it is found that it gradually diminishes, until a certain minimum is reached, and then it gradually increases (Table 43).

Table 43. The influence of 0.1 N HCl on the elec. conductivity.

c. c.	Good (0.465%) $k \times 10^3$	Mid. (0.380%) $k \times 10^3$	Bad (0.371%) $k \times 10^3$
0	0.5845	0.5189	0.5470
0.05	0.6116	0.5603	0.5641
0.1	0.5888	0.5312	0.5408
0.2	0.6164	0.5441	0.5931
0.3	0.6415	0.6171	0.6844
0.5	0.6861	0.7670	0.8267
0.7	0.8219	1.1046	1.1660
1.0	1.1718	1.5968	1.6306

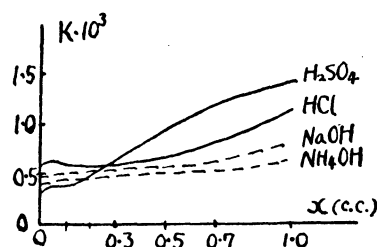


Fig. 18.

The minimum point of the electric conductivity is approximately at pH 4.10 which corresponds to the isoelectric point of sericin. Comparing it with the variation of electric conductivity on addition of acid it is the greatest for the sericin solution obtained from the cocoon of bad "kaijo."

If a base be gradually added to the sericin sol, the electric conductivity increases. The effect of alkali on the conductivity is also the greatest for the sericin solution of bad "kaijo." This may be due to the difference of buffer activity of sericin solutions. The buffer activity of sericin will be given later.

(5) Effect of Salts and Pupa on the Electric Conductivity.

Table 44.

The influence of salts on elec. conductivity ($k \times 10^3$).

c. c.	NaCl	CaCl ₂	MgCl ₂	AlCl ₃	FeCl ₃	Th(NO ₃) ₄
	(0.3%)	(0.34%)	(0.36%)	(0.36%)	(0.29%)	(0.39%)
0	0.3636	0.3931	0.4188	0.4188	0.3560	0.4753
0.05	0.3646	0.4759	0.3835	0.4221	0.3536	0.5262
0.1	0.3738	0.5521	0.3947	0.4610	0.3969	0.5367
0.2	0.4312	0.6698	0.4023	0.4641	0.4175	0.5442
0.3	0.4831	0.8069	0.4802	0.5845	0.4561	0.5636
0.5	0.5374	0.9662	0.5014	0.8051	0.5741	0.6467
0.7	0.6530	1.2150	0.6865	1.0562	0.7259	0.7239
1.0	0.7988	1.6731	0.9373	1.3722	1.0020	0.9122

(Conc. of salt solutions = 0.1 M.)

(a) **Salts.** In the low concentration of salts the changes of the electric conductivity of sericin solutions are shown in Table 44 and Fig. 19. The salts like CaCl₂ and AlCl₃ which affect remarkably the surface tension and viscosity, give also a stronger effect on the electric conductivity than other salts.

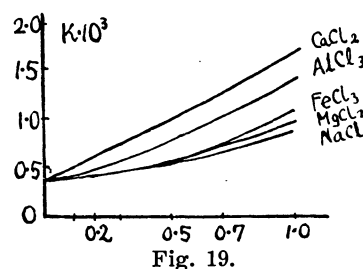


Fig. 19.

(b) **Pupa.** The sericin solution prepared by boiling cocoons containing the pupa with water has a very high value of electric conductivity. If the electric conductivity is only due to the presence of sericin salt and its micellar weight is 12000 for 0.37–0.23 per cent. solution, the degree of dissociation calculated is given in Table 45.

Table 45.

Conc. (%)	Spec. cond. $k \times 10^4$	Dilution V	Equivalent cond. λ_v	Degree of dissoc. $\alpha = \lambda_v / \lambda_\infty$
0.37	4.20	3200	1344	0.54
0.30	3.98	4000	1592	0.64
0.23	3.26	5200	1695	0.68
0.16	3.08	6000	1848	0.74
0.0	3.56	∞	2560	—

In the dilute sericin solution the degree of dissociation corresponds to about 0.60. It was already noticed that the degree of dissociation of sodium caseinate is 0.787 in 0.355 per cent. solution.

(To be continued).

THE FUSION CURVES OF THE SYSTEMS $\text{Br}_2\text{—CHCl}_3$,
 $\text{Br}_2\text{—CCl}_4$, AND $\text{CHCl}_3\text{—CCl}_4$.

By Jitsusaburo SAMESHIMA and Tatsuichi HIRAMATSU.

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The fusion curves of the systems between bromine and organic liquids were determined by Maass and McIntosh.⁽¹⁾ In the present paper the results of measurements of the freezing points of the systems $\text{Br}_2\text{—CHCl}_3$ and $\text{Br}_2\text{—CCl}_4$ as well as $\text{CHCl}_3\text{—CCl}_4$ are reported.

The pure samples of bromine, chloroform, and carbon tetrachloride from Merck were used. The carbon tetrachloride was further purified by crystallization, and the chloroform by shaking with sulphuric acid and then with potassium dichromate solution. The temperatures were measured by a pentane thermometer bearing the correction table from Physikalisch-Technische Reichsanstalt. About 20–30 grams of the liquid were taken in each measurement, and the temperature were recorded every 30 seconds. The freezing point was determined by means of the cooling curve thus drawn. The results are shown in Tables 1, 2 and 3. These data are depicted in Figures 1, 2 and 3.

(1) Maass and McIntosh, *J. Am. Chem. Soc.*, **34** (1912), 1273.

Table 1. $\text{Br}_2\text{--CHCl}_3$.

Mole% of Br_2	Freezing point	Mole % of Br_2	Freezing point
0.00	-63.5°C.	23.26	-45.7
3.78	-63.2	33.48	-41.0
8.72	-68.9	41.17	-35.0
10.92	-70.3	44.97	-32.7
12.66	-71.5	52.52	-27.8
14.15	-67.4	62.03	-23.5
15.14	-63.8	71.86	-18.8
17.85	-60.0	82.43	-14.5
19.23	-56.8	89.94	-12.0
20.72	-53.5	93.97	-9.7
24.35	-48.2	100.00	-7.3

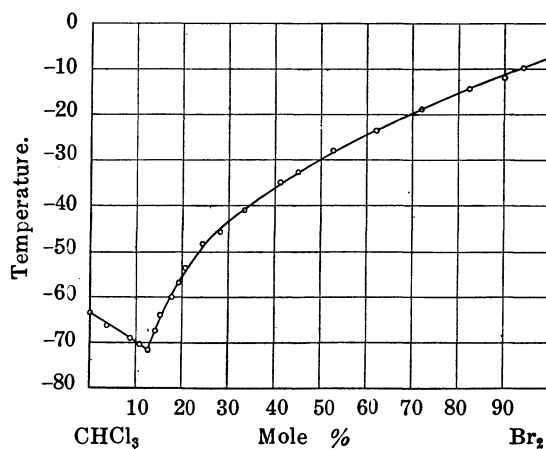


Fig. 1.

Table 2. $\text{Br}_2\text{--CCl}_4$.

Mole % of Br_2	Freezing point	Mole % of Br_2	Freezing point
0.00	-22.9°C.	32.08	-38.5
1.40	-24.3	40.60	-32.1
4.80	-30.0	46.50	-28.1
8.68	-36.4	55.32	-25.0
10.99	-42.0	62.11	-22.1
12.74	-44.6	67.49	-20.0
15.10	-47.5	74.38	-17.5
17.26	-47.6	79.78	-15.2
20.05	-46.7	85.09	-13.1
21.49	-45.8	92.20	-10.6
22.81	-44.8	96.50	-8.9
26.15	-40.8	100.00	-7.3

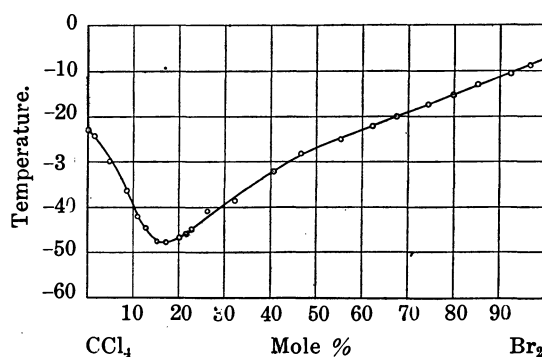


Fig. 2.

Table 3. $\text{CHCl}_3\text{--CCl}_4$.

Mole % of CHCl_3	Freezing point	Mole % of CHCl_3	Freezing point
0.00	-22.9°C.	51.03	-77.5
4.90	-28.5	53.96	-80.0
8.38	-35.5	56.12	-83.2
11.10	-40.8	58.30	-85.7
14.30	-45.3	59.13	-86.9
16.31	-52.0	60.51	-86.4
18.21	-55.7	62.24	-85.1
19.48	-55.3	65.25	-83.0
20.37	-55.8	67.84	-82.1
21.40	-56.5	71.23	-79.8
23.67	-57.1	76.61	-76.8
26.25	-58.2	80.34	-74.7
31.11	-61.3	85.58	-71.5
36.62	-65.2	89.69	-70.1
41.57	-63.1	92.78	-66.8
44.65	-71.7	96.15	-65.4
47.54	-74.6	100.00	-63.5

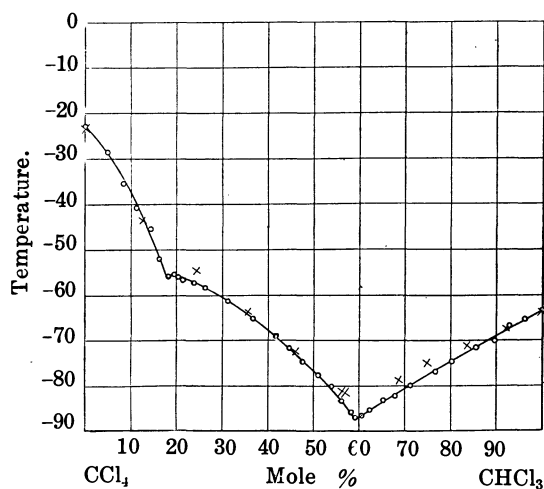


Fig. 3.

We see, from these figures, that there is no compound in the systems $\text{Br}_2\text{—CHCl}_3$ and $\text{Br}_2\text{—CCl}_4$. In the system $\text{CHCl}_3\text{—CCl}_4$, however, there is one compound $\text{CHCl}_3 \cdot 4\text{CCl}_4$, its melting point being -55°C .

Table 4.
 $\text{CHCl}_3\text{—CCl}_4$.
(Int. Crit. Tab.)

Weight % of CCl_4	Mole % of CHCl_3	Freezing point
100	0	-23.4°C .
90	12.5	-43.5
80	24.4	-54.5
70	35.6	-63.7
60	46.2	-72.4
50	56.3	-81.0
49.4	56.9	-81.4 (Eutectic pt.)
40	68.8	-78.6
30	75.0	-75.0
20	83.7	-71.2
10	92.1	-67.5
0	100.0	-63.7

The freezing points of the system $\text{CHCl}_3\text{—CCl}_4$ measured by Kanolt⁽²⁾ are given in the "International Critical Table." The data are shown in Table 4, and by crosses in Fig. 3.

The freezing point of carbon tetrachloride has recently been found to be -22.87°C . by Johnston and Long⁽³⁾ which coincides with our value -22.9°C ., but differs considerably from Kanolt's value -23.4°C .

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(2) International Critical Tables, Vol. IV (1928), p. 98.

(3) Johnston and Long, *J. Am. Chem. Soc.*, **56** (1934), 31.

A MICRO-METHOD FOR THE DETERMINATION OF DISULPHIDE-AND SULFHYDRYL-COMPOUNDS.⁽¹⁾ I.

By Hideo TOYODA.

Received May 9th, 1934. Published June 28th, 1934.

Introduction.

Biochemistry of sulphur has been paid much attention by various workers. And a number of methods for the determination of sulfhydryl (R-SH) and disulphide (R-S-S-R) compounds have been proposed. However, as it is well known, every one of these methods is subject to its own disadvantage, and none can be accepted as entirely dependable.

It is well known that sulphur plays an important rôle in its variously combined forms such as sulfhydryl (-SH), disulphide (-S-S-), sulfinate

($\begin{smallmatrix} \text{O} \\ | \\ -\text{S}-\text{OH} \end{smallmatrix}$), sulfoxide ($\begin{smallmatrix} \text{O} \\ | \\ -\text{S}- \end{smallmatrix}$), and sulphone ($\begin{smallmatrix} \text{O} \\ | \\ -\text{S}- \\ | \\ \text{O} \end{smallmatrix}$) groups, in the field of physiology of living tissue, especially in the process of proliferative growth mechanism. Therefore, in order to carry out further investigation of this problem in the realm of biochemistry, there is an acute necessity of establishing a dependable method for the determination of sulfhydryl (R-SH) compounds and their oxidation products, the disulphides (R-S-S-R), that will give accurate results.

In 1929, I. St. Lorant⁽²⁾ published his investigation on a micro-colorimetric method for the determination of hydrogen sulphide. Lorant's method is based upon Caro's methylene blue reaction.

In order to find out applicability of this principle of methylene blue reaction for the determination of R-SH and R-S-S-R compounds, and also to establish a new method thereby, the following experiments were carried out. It was found that dimethyl-*p*-phenylenediamine hydrochloride gave a distinct blue colour quite identical with that of methylene blue, with sulfhydryl compounds in acid solution of proper concentration in presence of ferric ammonium sulphate. The experimental results proved

(1) Read before the Monthly Meeting of the Chemical Society of Japan, March 10, 1934. H. Toyoda, "Observation on the new colour reaction of sulfhydryl compounds, and its application to the quantitative determination of cystine." *J. Chem. Soc. Japan*, **55** (1934), 272.

(2) I. St. Lorant. "Über eine neue colorimetrische Mikro-methode zur Bestimmung des Schwefels in Sulfiden, Sulfaten u.s.w.," *Z. physiol. Chem.*, **185** (1929), 245.

that the new method is available for the micro-determination of R—SH and R—S—S—R, i.e. cystine, cysteine, glutathione and thiocresol in blood, tissue, urine, and other biological substances. Tyrosine, tryptophane, uric acid, creatin and acetone do not interfere the test.

Experimental.

Reagents. (1) **Dimethyl-*p*-phenylenediamine hydrochloride solution.** Half a gram of dimethyl-*p*-phenylenediamine hydrochloride (Merck) was placed in a 1000 c.c. volumetric flask together with 100 c.c. distilled water, and 50 c.c. of concentrated sulphuric acid (sp. g. 1.84) was added directly, the temperature being kept low. Then, the mixture was diluted to the mark with distilled water also under cooling.

(2) **Ferric ammonium sulphate solution.** Twenty-five grams of ferric ammonium sulphate (Merck) was dissolved with 5 c.c. of concentrated sulphuric acid (sp. g. 1.84) in a 200 c.c. volumetric flask, and diluted to the mark with distilled water.

(3) **Cystine solution.** 1/2000 Molar solution of cystine was prepared by dissolving 0.12 g. of cystine (Merck) in 20 c.c. of 2 *N* HCl, and making up to 1000 c.c. with sulphur-free water. One c.c. of this solution contained 0.12 mg. of cystine.

(4) **Methylene blue solution.** In a 1000 c.c. volumetric flask, 0.032 g. of methylene blue (Merck) was placed, and dissolved in 20 c.c. of 2 *N* HCl, and then the whole was diluted to the mark with distilled water.

(5) **Normal HCl.** The solution was standardized against the normal NaOH.

(6) **Preparation of sulphur-free water.** The ordinary distilled water was made a little alkaline, and then distilled over potassium permanganate.

Procedure. The different amounts of the cystine solution of known concentration were placed in 50 c.c. graduated cylinders. Then, about 50 mg. of pure metallic zinc powder was introduced into each cylinder, and exactly 0.50 c.c. of the *N* HCl was added. Immediately after the HCl was added, 7.5 c.c. of dimethyl-*p*-phenylenediamine hydrochloride solution was introduced slowly into each cylinder. Finally, 0.5 c.c. of ferric ammonium sulfate was added with care.

The resulting solutions were diluted to 20, 25, and 50 c.c. with distilled water, according to the concentration of cystine, for the colorimetric read-

ings. The cylinders were well stoppered and set aside at room temperature for, at least, twelve hours before taking colorimetric readings.

The standard for the colorimetric readings was prepared with the cystine solution of known concentration. For this purpose 0.30 mg. or 0.60 mg. in 20 c.c. was found to be convenient concentration.

The Study of Establishing Proper Acidity of Test Solution. Since concentration of hydrochloric acid had much influence on the development of colour, a study was made to determine the concentration that would give maximum intensity. A series of experiments, using hydrochloric acid of varied concentrations, were carried out. Into two series of cylinders, 0.60 mg. and 1.20 mg. of cystine were introduced respectively, and 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, and 1.00 c.c. of the normal HCl were added to them

Table 1.

No. of cylinders	Volume of N HCl added c.c.	(A) Value of 20/R.	(B) Value of 20/R.
1	0.10	1.000	1.000
2	0.15	1.111	1.064
3	0.20	1.124	1.130
4	0.25	1.176	1.298
5	0.30	1.197	1.309
6	0.35	1.235	1.316
7	0.40	1.266	1.333
8	0.45	1.724	1.504
9	0.50	1.923	1.739
10	0.55	1.639	1.562
11	0.60	1.538	1.351
12	0.65	1.481	1.333
13	0.70	1.428	1.290
14	0.75	1.143	1.280
15	0.80	1.124	1.227
16	0.85	1.099	1.111
17	0.90	1.081	1.093
18	0.95	1.010	1.075
19	1.00	0.990	1.053

(A) Series. 0.60 mg. of cystine was used. Dilution volume....20 c.c.
The cylinder No. 1 was used as standard, set at 20 mm.

(B) Series. 1.20 mg. of cystine was used. Dilution volume....20 c.c.
The cylinder No. 1 was used as standard, set at 20 mm.

in the order of the cylinders, other conditions being exactly the same as described in procedure. At the end of 5, 6, 7, 12, and 24 hours, the colour intensity of each solution was studied, having cylinder No. 1 as the standard. The average values from a number of experiments are listed in Table 1. From these figures, it was obvious that the colour intensity varied with the different concentrations of hydrochloric acid, and it developed best in its intensity and shade when 0.50 c.c. of the normal HCl was added.

The Study of Colour Intensity with Varied Concentrations of Cystine. In order to prove the proportionality of the colour intensity with the concentration of cystine, the following experiments were carried out. Into a series of cylinders, different amounts of cystine were introduced, and they were treated according to the method described in procedure. The figures are listed in Tables 2 and 3. In the tables the experimental, and also the theoretical, ratios of the colour intensity are listed. The ratios obtained by the actual colorimetric comparison are listed in the column, "Value of 20/R."

The theoretical ratio means the value $\frac{\text{mg. weight of cystine used}}{\text{mg. weight of cystine used as St.}}$. As the standard for Table 2, 0.36 mg. of cystine was used, and 1.32 mg. of cystine was used as the standard for Table 3. In both series, the standards were set at 20 mm. for the colorimetric readings. The volumes of the final dilution with distilled water were 20 and 50 c.c. for Tables 2 and 3 respectively.

From the figures in the tables, it was shown that there was direct proportionality between the colour intensity and the concentration of cystine. Figs. 1 and 2 were plotted on the basis of Tables 2 and 3 respectively.

Table 2.

No. of cylinders	Weight of cystine in mg.	Value of 20/R.	Theoretical ratio
1	0.24	0.64	0.66
2	0.36	1.00	1.00
3	0.48	1.33	1.30
4	0.60	1.66	1.67
5	0.72	2.04	2.00
6	0.84	2.35	2.33
7	0.96	2.63	2.67
8	1.08	2.94	3.00
9	1.20	3.33	3.33

Standard—0.36 mg. cystine set at 20 mm. Dilution volume—20 c.c.

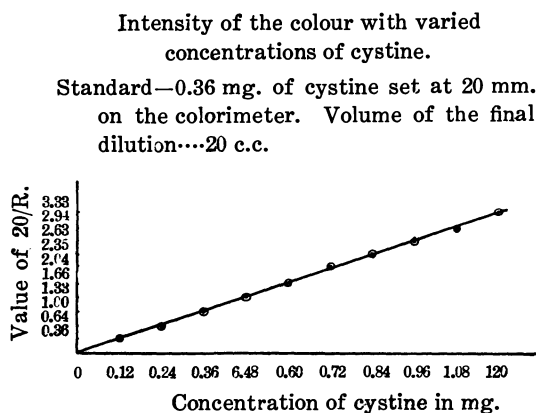


Fig. 1. (see Table 2).

Intensity of the colour with varied concentrations of cystine.
Standard—1.32 mg. of cystine set at 20 mm. in the colorimeter. Volume of the final dilution...50 c.c.

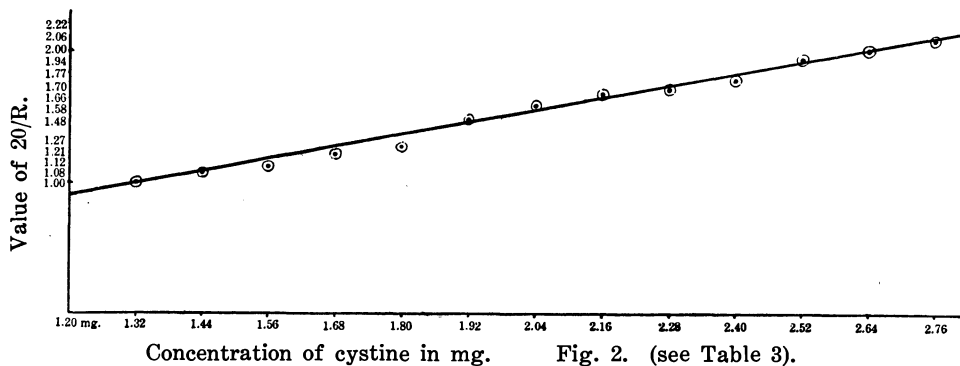


Fig. 2. (see Table 3).

Table 3.

No. of cylinders	Weight of cystine in mg.	Value of 20/R.	Theoretical Ratio
1	1.44	1.08	1.09
2	1.56	1.12	1.18
3	1.68	1.21	1.27
4	1.80	1.27	1.36
5	1.92	1.48	1.45
6	2.04	1.58	1.55
7	2.16	1.66	1.64
8	2.28	1.70	1.71
9	2.40	1.77	1.82
10	2.52	1.94	1.91
11	2.64	2.00	2.00
12	2.76	2.06	2.09
13	2.88	2.22	2.10
14	3.00	2.30	2.27

Standard—1.32 mg. cystine set at 20 mm. Dilution volume...50 c.c.

Study of Colour Intensity and its Relation to Time. In order to find the time required for development of the colour with the varied concentrations of cystine solution, a number of experiments were carried out. On the basis of average values obtained, at the different time intervals, Fig. 3 was drawn. For obtaining colorimetric readings, the present author used the stock methylene blue solution as the standard, treating it exactly same as the cystine solution. As it was seen from the Fig. 3, the reaction of the colour development was obviously slow, and quite gradual.

The results of the further investigations on the colour reaction will be reported in a separate paper.

Relation between colour intensity and time intervals.

— (A) 0.60 mg. (B) 1.20 mg.

Dilution volume...20 c.c. for both series. Methylene blue solution was used as the standard. Standard was set at 20 mm. on the colorimeter.

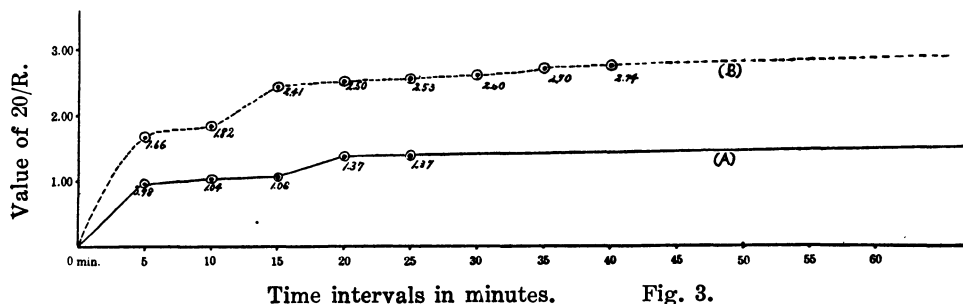


Fig. 3.

Summary.

A new micro-method for the determination of R—S—S—R (Cystine) and R—SH (Cysteine) is described, based on the fact that dimethyl-*p*-phenylenediamine hydrochloride gives a distinct methylene blue colour with R—SH compounds when the proper concentration of acid and of ferric ammonium sulphate are used. The colour thus obtained is permanent.

The advantages of this method are ease in determination, lack of interfering substances under normal biological conditions, and relative equivalence of R—SH and R—S—S—R groups.⁽³⁾

The author appreciates the advice and helpful criticism by Dr. K. Shinohara of the Research Institute of the Lankenau Hospital, Philadelphia.

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(3) The water extract of yeast gave a certain colour reaction to the test, and it suggested that vitamin B₁ in the yeast might have contained sulphur, of which chemical property is somewhat similar to that of R—SH or R—S—S—R compounds, in its complex chemical body.

CONCENTRATION OF DEUTERIUM BY ELECTROLYSIS OF SULPHURIC ACID SOLUTIONS.

By T. TITANI, K. KURANO, and M. HARADA.

Received June 18th, 1934. Published July 28th, 1934.

Since it was found that the electrolytical fractionation of water was very efficient to concentrate deuterium, experiments have been carried out in our laboratory to prepare heavy water by this method.

The present paper is concerned with the preliminary experiments on the electrolysis of sulphuric acid solutions with lead electrodes. The commercial sulphuric acid was diluted to 10 per cent. concentration with ordinary tap water and subjected to electrolysis using lead electrodes. The results are shown in Table 1.

Table 1.

Series	Initial volume c.c.	Final volume c.c.	Parts H ² per 1,000	α	a	b
1	6,400	100	0.8	2.2	1.50	0.62
2	50,000	1	9	2.7	1.54	0.78
3	61,000	7	7	2.4	1.58	0.62

The symbol α denotes the electrolytical separation coefficient defined by the following equation :

$$d \ln H^1 = \alpha d \ln H^2 .$$

The meanings of a and b will be explained later.

The electrolyzing apparatus was very simple. Tall beakers of about 200 c.c. capacity, 5 cm. diameter, and 10 cm. height, were used as cells. They were filled with the electrolyte and placed in series in running water. The lead electrodes employed consisted of 2 sheets of plates 10 cm. long and 4 cm. wide, which were joined together by a thin strip of lead plate; one sheet formed the anode and the other the cathode in neighbouring cells. The cells were put in series in D. C. of about 4 amperes obtained either from a motor generator or from rectifiers. Upon reaching half the original volume the content of a cell was first neutralized with Na_2CO_3 , distilled, and then added to the other cells with contents of the same order of concentration as the one to be added. This process was repeated until the final

product was obtained. The density of the final products, after being carefully purified, was measured by means of a pycnometer or by a bouyancy balance.

In order to find the electrolytical separation coefficient α from the data thus obtained, it must be taken into consideration that fairly large amounts of the solution were lost during electrolysis owing partly to evaporation and partly to escaping sprays resulting from bubbles at electrodes. The loss due particularly to the latter factor was appreciably large in the arrangement employed by us. In order to minimize this loss, a watch glass was placed on each cell. It may be justified in stating that the amount of loss due to evaporation and escaping sprays is proportional to the total number of cells and this is again proportional to the total amount of the solution present. And in the second place, it may be assumed that the isotopic composition of the lost solution is identical with that of the solution in the cells. Therefore, the total loss of protium and deuterium during electrolysis can be expressed by the two following terms instead of an usual single term :

$$-dN_1 = k_1 N_1 dt + K(N_1 + N_2) \frac{N_1}{(N_1 + N_2)} dt ,$$

$$-dN_2 = k_2 N_2 dt + K(N_1 + N_2) \frac{N_2}{(N_1 + N_2)} dt ,$$

where the second term in each differential equation stands for the loss due to both evaporation and spray-formation, N_1 and N_2 the total moles of protium and deuterium respectively, and K is a constant for both evaporation and spray-formation. Hence, on integrating these two equations, we can obtain the total separation coefficient α :

$$\alpha = \frac{\ln N_{10} - \ln N_1}{\ln N_{20} - \ln N_2} = \frac{k_1 + K}{k_2 + K} \dots\dots\dots (1),$$

where N_0 indicates the values at the commencement of electrolysis. Here, it should be mentioned that, since we started with ordinary tap water, the ratio of total moles of deuterium to that of protium was taken as one part to 5,000.

However, as the ordinary water may be considered to consist of pure protium water, the ratio of its loss due to evaporation and spray-formation (W) to that due to pure electrolysis (E) should be equal to the ratio K/k_1 :

$$W/E = K/k_1 = b \dots\dots\dots (2).$$

The value b can be easily found experimentally from the total and the

theoretical losses during the electrolysis. From equations (1) and (2) we can obtain the electrolytical separation coefficient α as follows :

$$\alpha = \frac{k_1}{k_2} = \frac{a}{1-b(a-1)} \dots\dots\dots (3).$$

The values a , b and α obtained in this way are given in Table 1.

Our results can be compared with those of Collie⁽¹⁾ who electrolyzed 10 per cent. ordinary sulphuric acid solution using lead electrodes and obtained the electrolytical separation coefficient $\alpha = 1.2-3.8$, which is quite close to ours. Some other authors used more dilute solutions of sulphuric acid. For instance, Erlenmeyer and Gärtner⁽²⁾ started from 8 liters of ordinary 0.1 *N* sulphuric acid and obtained 13 c.c. of heavy water containing 5 parts H² per 1000. From this result it will be seen that α is 2.0, neglecting the loss due to evaporation and spray-formation. The concentration of sulphuric acid does not seem to have much influence upon the separation efficiency. More recently Topley and Eyring⁽³⁾ made careful experiments on the separation efficiencies by electrolysis and obtained α as high as 6.2—6.6 by using 0.5 *N* sulphuric acid and lead electrodes. The discrepancy between this and values obtained by other observers is considerable. But it must be taken into consideration that the above-mentioned investigators started with more concentrated heavy water instead of ordinary water. It may be plausible that the magnitude of α depends upon the isotopic composition of starting materials. It might be of interest to confirm this view.

The experiments on electrolytic concentration, which are now being continued by using alkaline solutions and neutral salt solutions, will be published later.

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(1) C. H. Collie, *Nature*, **132** (1933), 568.

(2) H. Erlenmeyer and H. Gärtner, *Helvetica Chim. Acta*, **17** (1934), 30.

(3) B. Topley and H. Eyring, *J. Chem. Phys.*, **2** (1934), 217.

CONCENTRATION OF DEUTERIUM BY ELECTROLYSIS OF NEUTRAL SALT SOLUTIONS. I.

By T. TITANI, K. OKABE, and M. HARADA.

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One of the most efficient methods of concentrating deuterium is the electrolytical fractionation of either caustic alkali solutions with nickel electrodes⁽¹⁾ or sulphuric acid solutions with lead electrodes.⁽²⁾ The theories expounded in order to explain the mechanism of separation do not well agree with one another. However, it is well known that separation occurs at the cathode. For example, when NaOH is used as the electrolyte, the important rôle played by Na is that, upon reaching the cathode, it induces the separation of deuterium from protium. Hence, separation may also be effected by employing a neutral sodium salt as the electrolyte.

From this point of view, a preliminary experiment was carried out to effect the separation by using a 0.25 mol solution of Na₂SO₄, the solvent being ordinary tap water. Seven liters of this solution were subjected to electrolysis between a nickel cathode and a lead anode, both being 10 cm. long and 4 cm. wide. A current of 2.5 amperes was passed through. Experimental procedure was the same as described in the preceding paper,⁽³⁾ except that the electrolyzed solution was distilled without neutralization in this case, though the solution was found to be slightly alkaline after the electrolysis, presumably owing to the disappearance of SO₄''-ions at the lead-anode. The final product of about 134 c.c. was carefully purified and the determination of density by a quartz bouyancy balance showed that this final product contained 0.85 part H² in 1,000. Assuming the initial concentration to be 1 part H² in 5,000, the total separation coefficient was found to be $\alpha = 1.58$.⁽⁴⁾ However, the factor b , which is the ratio of the loss due to the evaporation and spray-formation to that of the pure electrolysis, was found to be 0.58. Hence, the electrolytical separation coefficient α was calculated by the equation :

(1) G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.*, **1** (1933), 341; H. S. Taylor, H. Eyring, and A. A. Frost, *J. Chem. Phys.*, **1** (1933), 823; R. P. Bell and J. H. Wolfenden, *Nature*, **133** (1934), 25; B. Topley and H. Eyring, *J. Chem. Phys.*, **2** (1934), 217; etc.

(2) C. H. Collie, *Nature*, **132** (1933), 568; K. F. Bonhoeffer and G. W. Brown, *Z. physik. Chem. (B)*, **23** (1933), 171; H. Erlenmeyer and H. Gärtner, *Helvetica Chim. Acta*, **17** (1934), 30; B. Topley, H. Eyring, loc. cit., etc.

(3) P. 269 of this volume.

(4) For the method of calculation refer to the preceding paper.

$$\alpha = \frac{a}{1-b(a-1)},$$

and found to be 2.3.

Therefore, the separation efficiency by the use of Na_2SO_4 with a nickel cathode is quite close to that of 10 per cent. sulphuric acid with a lead cathode ($\alpha = 2.2-2.7$) as was reported in the preceding paper. For the sake of comparison the electrolysis was carried out by using a 0.5 mol NaOH solution with nickel electrodes and a current intensity of 3 amperes. The result is as follows: initial volume = 6,000 c.c., final volume = 100 c.c., part of H^2 in 1,000 = 0.8, $\alpha = 1.52$, and $b = 0.88$, hence $\alpha = 2.8$. The separation efficiency is approximately equal to that with a Na_2SO_4 solution.

There are at least two distinct advantages in using the neutral salts over acid or alkaline solutions: namely, first, it dispenses with the process of neutralization, thereby saving considerably amount of labour and time; secondly, the same electrolyte can be used throughout. The full report on the final results will be published shortly, as the process of separation are at present being carried on along the lines reported so far.

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UNTERSUCHUNGEN ÜBER DIE OXYDASENARTIGEN
WIRKUNGEN GEWISSE METALL-
KOMPLEXSALZE. X.

Von Yuji SHIBATA und Kazuo YAMASAKI.

Eingegangen am 23. Juni, 1934. Ausgegeben am 28. Juli, 1934.

Im Jahre 1918 wurde von K. Shibata und Y. Shibata eine interessante Beobachtung über das oxydaseartige Verhalten gewisser Metallkomplexsalzen angestellt, und seither wurde eine Reihe von experimentellen, insbe-

sondere reaktionskinetischen Untersuchungen dieser Erscheinung von den genannten Autoren und ihren Mitarbeitern⁽¹⁾ vielfach mitgeteilt.

Die Substrate, die bisher in diesbezüglichen oxydativen Versuchen gebraucht wurden, waren immer Polyphenole, deren OH-Gruppen sich besonders leicht von Metallkomplexsalzen angreifbar erwiesen. In vorliegender Arbeit wird aber die Oxydation von einem Aminophenol, d.h. N-methyl-*p*-aminophenolsulfat (Metol), durch verschiedene Komplexsalze von Kobalt und Chrom näher studiert.

Da die wässrige Lösung des Metols (N-methyl-*p*-aminophenolsulfat) merklich sauer reagiert und das Oxydationsvermögen von Metallkomplexsalzen durch Säuren stark verzögert wird, so wurden die Versuchsgemische mit einer Pufferlösung von $pH=9.4$ versetzt, um die Lösung schwach alkalisch reagieren zu lassen.

Wie weiter unten im experimentellen Teil angegeben, absorbiert die schwach alkalisch gemachte Metollösung an sich selbst den Sauerstoff und durch Versetzung eines Komplexsalzes wird diese Autoxydation im Gegensatz zum Falle gewöhnlicher Polyphenole, vielmehr mehr oder minder gehemmt, indem etwaige Niederschläge immer zwischen Metol und Komplexsalze gebildet werden. Dabei ist es sehr interessant zu bemerken, dass die Intensität dieser verzögernden Wirkung der Metallkomplexsalze auf die Autoxydation des Metols in ganz gleicher Reihenfolge zu der beschleunigenden bei der Oxydation von Polyphenolen steht; nämlich wirken solche Komplexsalze, welche auf Polyphenole am stärksten oxydativ wirksam sind, auch am bedeutendsten verzögernd auf die Autoxydation von Metol.

(1) 1. Y. Shibata und K. Shibata, Untersuchungen über die oxydasenartigen Wirkungen gewisser Metallkomplexsalze. *J. Chem. Soc. Japan*, **41** (1920), 35; *Acta Phytochimica*, **4** (1929), 363.

2. K. Shibata, Über die Wirkungsmechanismus der oxydoreduktiven Enzyme. *Acta Phytochimica*, **4** (1929), 373.

3. Y. Shibata u. H. Kaneko, Kinetik der katalytischen Oxydation durch gewisse Metallkomplexsalze. *J. Chem. Soc. Japan*, **43** (1922), 833; *Chem. Abst.*, **17** (1923), 2811.

4. Y. Shibata u. H. Kaneko, Hydroperoxydzersetzung durch gewisse Metallkomplexsalze. *J. Chem. Soc. Japan*, **44** (1923), 166; *Chem. Abst.*, **17** (1923), 2812.

5. H. Kaneko, Eigenschaften der wässrigen Lösungen einiger Kobaltkomplexsalze. *J. Chem. Soc. Japan*, **48** (1927), 391; **49** (1928), 380; **54** (1933), 259.

6. A. Watanabe, Jodidoxydation durch Metallkomplexsalze. *J. Chem. Soc. Japan*, **49** (1928), 476; *Chem. Abst.*, **22** (1928), 3431; Über die vitale Oxydation der Pflanzenzellen mit den Kobaltaminkomplexsalzen. *Japanese J. of Botany*, **4** (1928), 31.

7. Y. Shibata u. R. Tsuchida, Studies on Asymmetric Oxidation, I. (prelim. note). *This Bulletin*, **4** (1929), 142.

8. Y. Shibata, Y. Tanaka, u. S. Goda, Studies on the Asymmetric Oxidation, II. *This Bulletin*, **6** (1931), 210.

9. Y. Shibata u. S. Goda, The Action of Light on Catalytic Oxidation by Some Metallic Complex Salt. *This Bulletin*, **6** (1931), 217.

Von dieser Tatsache aus, kann man wohl den Schluss anziehen, dass für die oxydationskatalytische Wirkung von Metallkomplexsalzen eine vorübergehende Vereinigung zwischen denselben und den Substraten erforderlich ist, und zwar ergeben die Metallkomplexe desto leichter die Molekülverbindungen mit dem Substrat, je stärker sie oxydierend einwirken vermögen. Da aber solche Molekülverbindungen zwischen Kobaltkomplexe und Metol unlöslich sind und folglich sofort vom Reaktionskreis ausgeschieden werden, so scheint es, dass die stärksten Oxydatoren für Phenole gerade die bedeutendste Hemmung der Autoxydation von Metol bewirken.

Weiterhin wurde die Beeinflussung der in Betracht kommenden Vorgänge durch einige Substanzen studiert, welche auf die katalytischen Oxydation der Phenole durch Kobaltkomplexe immer hemmend einwirken, so z. B. Chromkomplexe,⁽²⁾ Kaliumcyanid und Hydroxylamin.

Beschreibung der Versuche.

Der Sauerstoffverbrauch wurde mit zwei Warburgschen Manometern messend verfolgt. Die Volumen der beiden Reaktionsgefäße betrugen je 50.8 c.c. und 50.7 c.c., und diese zwei Manometern wurden gänzlich ins Wasser der Thermostat (25°C.) eingetaucht, um den Temperatureinfluss auf Gasvolumen möglichst gut auszuschliessen.

Als Sperrflüssigkeit diente wie gewöhnlich die Brodielösung und die Schüttelungszahlen des Apparates war 50/min. .

Das käufliche N-methyl-*p*-aminophenolsulfat (Metol) wurde aus Wasser zweimal umkrystallisiert, während die unten bezeichneten Metallkomplexsalze von den Autoren selbst bereitet wurden.

[Co(NH₃)₆]Cl₃, [Co(NH₃)₅H₂O]Cl₃, [Co(NH₃)₅Cl]Cl₂, [Co(NH₃)₅SCN]Cl₂,
[Co(NH₃)₅NO₂]Cl₂, [Co(NH₃)₄CO₃]NO₃, [Co(NH₃)₄OH(H₂O)]SO₄,
[Co(NH₃)₄Cl(H₂O)]SO₄, [Co(NH₃)₄(NO₂)₂]Cl (Flavo u. Croceo),
[Co(NH₃)₃(NO₂)₃], [Co(NH₃)₂(NO₂)₄]NH₄·H₂O,
[Co(NH₃)₂(NO₂)₂(C₂O₄)]NH₄·H₂O, [Cr(NH₃)₅Cl]Cl₂,
[Cr(NH₃)₅SCN](SCN)₂, [Cr(C₂O₄)₃]K₃·3H₂O.

Das Gemisch von NH₄OH (0.046 *N*) und NH₄Cl (0.050 *N*) zu gleichen Teilen wurde als Pufferlösung (pH 9.4) verwendet.

(2) Chromkomplexe sind im allgemeinen sehr beständig in wässrigen Lösungen und oxydativ unwirksam. Wenn solche Komplexe vorher der Substratlösung zugesetzt wird, dann wird das Oxydationsvermögen von der nachher zugefügten wirksamen Komplexsalze bedeutend gehemmt. (Siehe Y. Shibata und K. Shibata, loc. cit.)

(I) Autoxydation von N-methyl-*p*-aminophenolsulfat; Kontrollversuch.

Das Versuchsgemisch bestand aus :

Substrat	1/500 M.	2 c.c. }	Hauptraum
30%ige KOH (in Einsatz)		1 c.c. }	
Pufferlösung		2 c.c. }	Ansatzbirne
Wasser		2 c.c. }	

(II) Sauerstoffaufnahme von Metollösung in Gegenwart von Komplexsalzen. (Siehe Tabelle 1 und Abb. 1 u. 2.)

Versuchsgemisch :

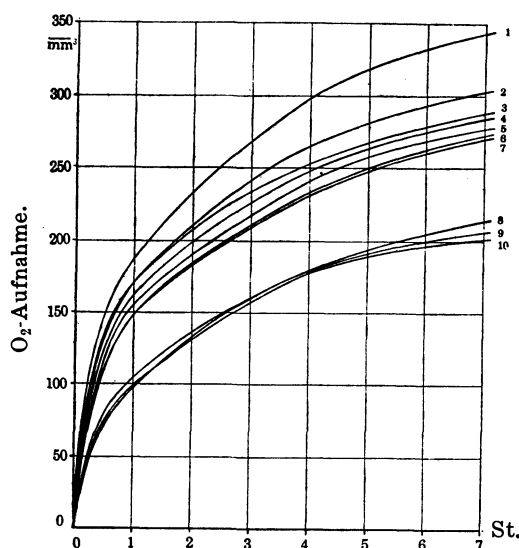
Substrat	1/500 M.	2 c.c. }	Hauptraum
30%ige KOH (in Einsatz)		1 c.c. }	
Pufferlösung		2 c.c. }	Ansatzbirne
Komplexsalzlösung	1/400 M. ⁽³⁾	2 c.c. }	

Tabelle 1.

Zeit	Metol	Metol + Komplexsalz															
	(1) ⁽⁴⁾	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
St.	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³
1/2	153	141	135	141	141	120	126	74	86	86	125	137	139	151	137	165	157
1	190	179	179	169	157	155	151	97	103	97	151	153	163	161	186	187	191
1 1/2	209	191	188	175	171	161	162	115	118	114	165	172	171	173	204	204	216
2	228	209	208	193	183	181	178	136	135	129	181	190	191	190	221	222	238
2 1/2	251	228	220	209	204	199	196	148	148	146	198	208	202	216	242	243	258
3	270	242	234	227	218	210	209	162	161	159	212	220	216	224	256	260	278
3 1/2	286	255	244	238	230	224	220	172	173	—	224	230	232	238	272	276	286
4	298	266	252	248	242	—	233	180	180	—	232	240	242	248	286	290	304
4 1/2	312	276	260	258	250	244	242	188	187	186	240	246	252	254	296	300	315
5	320	282	270	266	256	252	250	194	191	192	246	254	258	262	—	—	324
5 1/2	328	287	274	272	268	259	256	200	197	194	—	258	266	266	—	—	330
6	334	294	282	—	272	263	260	205	203	196	—	264	270	274	320	326	336
6 1/2	340	300	286	—	274	268	268	210	204	198	—	266	—	276	326	331	242
7	343	302	288	286	278	272	270	—	205	201	262	270	278	278	330	334	344

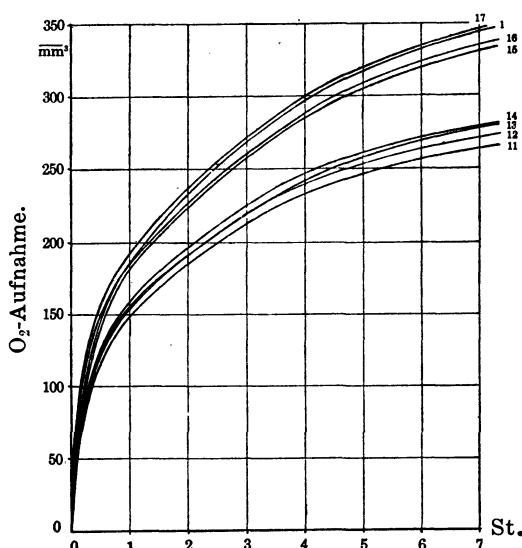
(3) Mit Ausnahme von $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/800 M.

(4) Diese Nummer sind dieselben wie die in den Kurven in Abb. 1 und 2 angegebenen.



- Kurve. 1. Substrat + Pufferlösung.
(Kontrollversuch).
2-17. Oxydation in Gegenwart von
Komplexsalze.
2. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
 3. $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$
 4. $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]\text{NH}_4$
 5. $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$, Flavo.
 6. $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$, Croceo.
 7. $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$
 8. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 9. $[\text{Co}(\text{NH}_3)_4\text{OH}(\text{H}_2\text{O})]\text{SO}_4$
 10. $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{H}_2\text{O})]\text{SO}_4$

Abb. 1.



- Kurve. 11. $[\text{Co}(\text{NH}_3)_5\text{SCN}]\text{Cl}_2$
12. $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$
13. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$
14. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
15. $[\text{Cr}(\text{NH}_3)_5\text{SCN}](\text{SCN})_2$
16. $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{K}_3$
17. $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
1. Kontrollversuch.

Abb. 2.

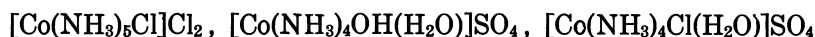
Durch Hinzufügen von Kobaltkomplexsalz zur Substratlösung tritt ein sofortiger Farbumschlag ins Braun ein und nach einigen Stunden wird schwarzer Niederschlag gebildet. Bemerkenswert ist hierbei, dass die Sauerstoffaufnahme dieser Reaktionsgemische immer geringer ist als die des Kontrollversuchs.

Der eben erwähnte schwarze Niederschlag ist pulverig, leicht löslich in Alkali und konz. Ammoniak, schwer in heissen Schwefelsäure und Salpetersäure und unlöslich in organischen Lösungsmitteln. Der Niederschlag enthält Kobalt und Stickstoff, dessen Anwesenheit durch Erhitzen mit Natronkalk nachgewiesen wurde. Es ist also höchst wahrscheinlich, dass diese Niederschläge aus den unlöslichen Molekülverbindungen zwischen den Kobaltkomplexsalzen und dem Substrat bestehen. Da ein Teil der Sub-

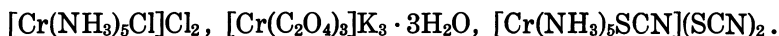
stratmenge auf diese Weise von der Lösung entzogen wird, so macht es sich ganz verständlich, dass die Sauerstoffaufnahme der Metollösung durch Zusatz von Kobaltkomplexen immer geringer wird als die des Kontrollversuchs.

Nach der Grösse der beobachteten Sauerstoffaufnahme werden die untersuchten Komplexsalze in 3 Gruppen eingeteilt.

(a) Die Kobaltkomplexsalze, die beim Zusammenbringen mit Metollösung die Fällung schon nach 1/2–1/3 Stunden verursachen. Die Sauerstoffabsorption dieser Gemische sind immer sehr gering, trotzdem die Komplexe dieser Art als die stärksten Oxydatoren auf Polyphenole galten.⁽⁵⁾



(b) Die Chromkomplexsalze, welche beim Zufügen zu Metollösung keinen Niederschlag ergaben und deswegen ihre Sauerstoffaufnahmen ungefähr gleich mit der des Kontrollversuchs sind.



(c) Diejenigen Kobaltkomplexsalze, welche nach bisherigen Untersuchungen als schwache Oxydatoren klassifiziert wurden, scheinen auch in jetzigem Falle nur eine geringe Bindungskraft gegen das Substrat zu zeigen, so dass die Fällung erst nach etwa 2–4 Stunden zur Erscheinung kommt und die Sauerstoffaufnahme dementsprechend wenig gehemmt wird.

(III) Die Einflüsse von einigen Substanzen, die auf die Oxydationswirkung der Komplexsalze hemmend einwirken.

Genau so wie bei Oxydationsenzymen, erleiden die Metall-Komplexsalze die Hemmung von ihren Wirkungen durch verschiedene Substanzen, wie Säuren, Cyanide, Sublimat, Hydroxylamin u. a. Hier sollen die Einflüsse der Anwesenheit solcher Verbindungen auf die in Frage kommenden Vorgänge näher untersucht werden.

(a) Einfluss der oxydativ unwirksamen Chromkomplexsalze.

Wenn man die Kobaltkomplexsalzlösung mit einem oxydativ unwirksamen Chromkomplexsalze versetzt und alsdann dieses Gemisch zur Metollösung zufügt, wird die Wirkung des Kobaltsalzes um so mehr untergedrückt, je grösser ist die Menge des zugefügten Chromsalzes. Siehe Tabelle 2 und Abb. 3.

Versuchsgemisch :

Chromkomplexsalz wurde in Kobaltkomplexsalzlösung gelöst.

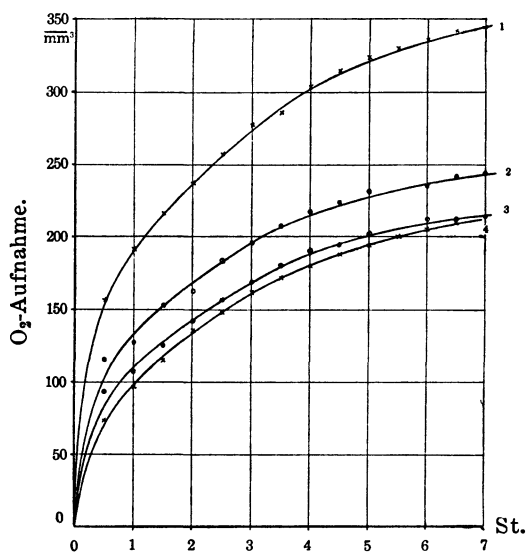
Substrat	1/500 M.	2 c.c. }	Hauptraum
30%ige KOH (in Einsatz)		1 c.c. }	

(5) Shibata u. Kaneko, loc. cit.

• Pufferlösung
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M. 2 c.c. } Ansatzbirne
 $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 od. 1/800 M. } 2 c.c.

Tabelle 2.

Zeit	$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	
	1/400 M.	1/800 M.
St.	mm ³	mm ³
1/2	115	93
1	127	107
1 1/2	153	125
2	163	142
2 1/2	183	157
3	196	169
3 1/2	208	180
4	218	190
4 1/2	224	194
5	232	202
6	236	210
6 1/2	242	212
7	244	214



Kurve. 1. Substrat + $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 (Abb. 2. Kurve. 17.)
 2. Substrat + $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 3. Substrat + $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/800 M.
 + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 4. Substrat + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 (Abb. 1. Kurve. 8.)

Abb. 3.

(b) Kaliumcyanid.

Da die wässrige Lösung des KCN ziemlich stark alkalisch ist und Metollösung selbst sauer reagiert, so verwendet man in diesem Falle keine Pufferlösung. Die Konzentration des KCN ist 1/100, 1/200, und 1/400 M.

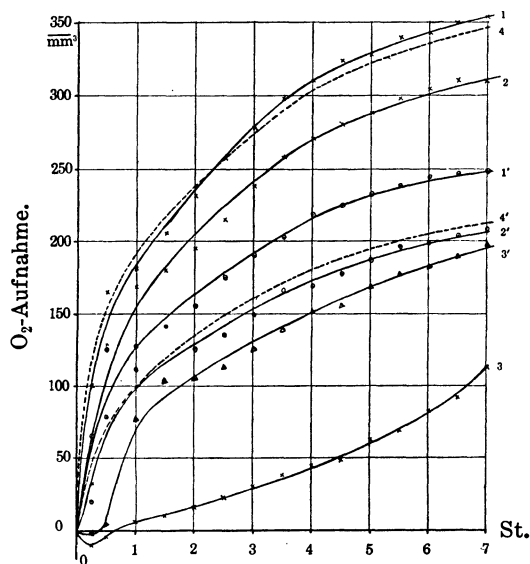
Versuchsgemisch :

Substrat 1/500 M. 2 c.c. } Hauptraum
 30%ige KOH (in Einsatz) 1 c.c. }
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M. 2 c.c. } Ansatzbirne
 KCN 2 c.c. }

Im Kontrollversuch wurde an Stelle der Komplexsalzlösung reines Wasser angewandt. Die hemmende Wirkung des Kaliumcyanides steht der von Chromsalzen merklich nahe. Siehe Tabelle 3 und Abb. 4.

Tabelle 3.

Zeit	Metol			Metol+[Co(NH ₃) ₅ Cl]Cl ₂		
	KCN			KCN		
	1/100 M.	1/200 M.	1/400 M.	1/100 M.	1/200 M.	1/400 M.
St.	mm ³	mm ³	mm ³	mm ³	mm ³	mm ³
1/4	100	32	—10 ⁽⁶⁾	65	20	—2
1/2	165	129	— 4	125	79	4
1	181	169	6	127	111	77
1 1/2	205	180	10	141	—	103
2	231	195	16	155	125	105
2 1/2	257	215	22	175	135	113
3	278	238	30	190	149	125
3 1/2	298	258	38	202	166	139
4	310	270	44	218	169	151
4 1/2	324	280	48	224	178	155
5	328	288	62	232	188	169
5 1/2	340	298	69	238	196	178
6	342	304	82	244	198	182
6 1/2	350	310	92	246	204	190
7	354	310	113	254	208	198



- Kurve. 1. Substrat + KCN 1/100 M.
 2. „ + „ 1/200 M.
 3. „ + „ 1/400 M.
 4. „ + Pufferlösung.
 (Abb. 1. Kurve. 1.)
 1'. Substrat + KCN 1/100 M.
 + [Co(NH₃)₅Cl]Cl₂ 1/400 M.
 2'. Substrat + KCN 1/200 M.
 + [Co(NH₃)₅Cl]Cl₂ 1/400 M.
 3'. Substrat + KCN 1/400 M.
 + [Co(NH₃)₅Cl]Cl₂ 1/400 M.
 4'. Substrat + Pufferlösung
 + [Co(NH₃)₅Cl]Cl₂ 1/400 M.
 (Abb. 1. Kurve. 8.)

Abb. 4.

(6) Die Konzentration von H₂SO₄ im Substrat ist 1/250 N. und grösser als die von KCN 1/400 M., also wird diese Druckzunahme durch Entwicklung von HCN-Gas verursacht. Dadurch wird auch die spätere Sauerstoffabsorption scheinbar herabgesetzt.

(c) Hydroxylamin.

Die Konzentration von Hydroxylaminhydrochlorid ist 1/100, 1/250, und 1/500 M. Siehe Tabelle 4 und Abb. 5.

Tabelle 4.

Zeit	Metol			Metol + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$		
	$\text{NH}_2\text{OH} \cdot \text{HCl}$			$\text{NH}_2\text{OH} \cdot \text{HCl}$		
	1/100 M.	1/250 M.	1/500 M.	1/100 M.	1/250 M.	1/500 M.
St.	mm^3	mm^3	mm^3	mm^3	mm^3	mm^3
$\frac{1}{4}$	100	87	105	85	75	58
$\frac{1}{2}$	199	188	207	163	159	137
1	329	290	255	176	182	149
$1\frac{1}{2}$	370	313	276	214	188	—
2	387	328	292	220	197	176
$2\frac{1}{2}$	394	342	308	224	207	185
3	399	350	320	234	220	203
$3\frac{1}{2}$	403	354	329	244	228	212
4	410	362	340	252	236	224
$4\frac{1}{2}$	416	366	346	255	244	230
5	420	371	350	258	251	236
$5\frac{1}{2}$	420	375	354	265	255	238
6	423	375	357	265	259	247
$6\frac{1}{2}$	427	379	362	267	265	249
7	430	381	365	269	265	249

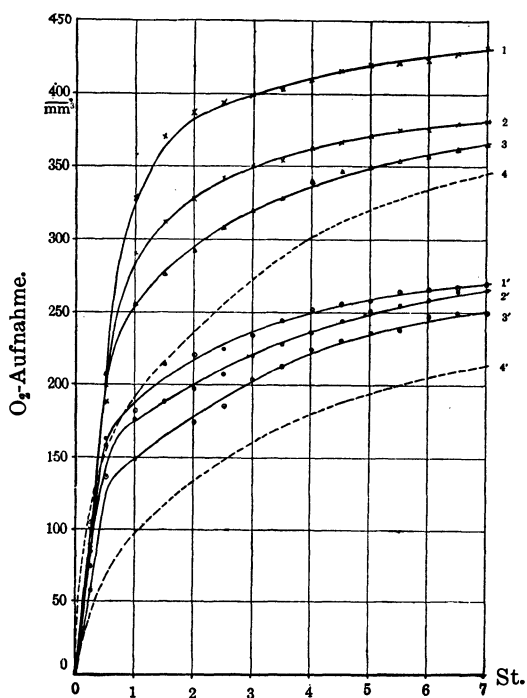


Abb. 5.

- Kurve. 1. Substrat+Hydroxylaminhydrochlorid 1/100 M.
 2. Substrat+Hydroxylaminhydrochlorid 1/250 M.
 3. Substrat+Hydroxylaminhydrochlorid 1/500 M.
 4. Substrat+Pufferlösung (Abb. 1. Kurve. 1.)
 1'. Substrat+Hydroxylaminhydrochlorid 1/100 M. + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 2'. Substrat+Hydroxylaminhydrochlorid 1/250 M. + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 3'. Substrat+Hydroxylaminhydrochlorid 1/500 M. + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M.
 4'. Pufferlösung + $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 1/400 M. (Abb. 1. Kurve. 8.)

Versuchsgemisch :

Substrat	1/500 M.	2 c.c.	} Hauptraum
30%ige KOH (in Einsatz)		1 c.c.	
Hydroxylaminhydrochlorid		1 c.c.	
Pufferlösung		2 c.c.	} Ansatzbirne
[Co(NH ₃) ₅ Cl]Cl ₂	1/400 M.	2 c.c.	
(im Kontrollversuch reines Wasser)			

Durch Zusatz von Hydroxylamin wird die Sauerstoffabsorption der Metollösung stark vermehrt, während die Hemmung der letzteren durch Kobaltkomplexe von der Menge des zugesetzten Hydroxylamin stets unabhängig ist. Die Erklärung für diese unerwartete Erscheinung könnte man vielleicht darin finden, dass irgendeine Molekülverbindung zwischen Hydroxylamin und Metol gebildet wird und diese letztere auf die Autoxydation des Metols beschleunigend einwirkt.

Zur Kontrolle wurde Hydroxylamin zu solchen Lösungen zugefügt, die einmal nur Pufferlösung und andermal Puffer und Komplexsalz zugleich enthalten; jedoch bei diesen beiden Fällen wurde keine Sauerstoffabsorption beobachtet.

Zusammenfassung.

1. Die Einflüsse von verschiedenen Kobalt- und Chromkomplexsalzen über die Autoxydation des N-methyl-*p*-aminophenolsulfat (Metol) wurden durch die Messung von absorbiertem Sauerstoff untersucht.

2. In Gegenwart von Kobaltkomplexsalzen wird die absorbierte Sauerstoffmenge im allgemeinen bedeutend herabgesetzt; also wird die Autoxydation des Metols durch Kobaltkomplexsalze scheinbar gehemmt und zwar wirkt auf die Sauerstoffaufnahme der Metollösung der stärkste Oxydator für Polyphenole (z.B. [Co(NH₃)₅Cl]Cl₂, [Co(NH₃)₄Cl(H₂O)]SO₄ u.a.) am bedeutendsten und der schwächste Oxydator für Polyphenole (z.B. [Co(NH₃)₆]Cl₃) am geringsten hemmend ein.

3. Chromkomplexsalze, die sich bei der Oxydationsbeschleunigung von Polyphenolen fast unwirksam aufweisen, verhalten sich in diesem Falle gleichfalls indifferent.

4. Gewisse Substanzen, die auf die katalytische Wirkung der Kobaltkomplexsalze bei der Oxydation von Polyphenolen hemmend einwirken, zeigen hier auch ähnliches Verhalten; so z.B. durch Zusatz von Chromkomplexsalzen oder Kaliumcyanid wird die Hemmungswirkung der Kobaltkomplexe auf die Metoloxxydation mehr oder minder deutlich beseitigt.

5. Hydroxylamin verhält sich hierbei etwas sonderlich ; nämlich wird die Autoxydation der Metollösung in seiner Gegenwart stark beschleunigt, während deren Hemmung durch Kobaltkomplexe dadurch kaum beeinflusst wird.

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THE COLLOIDAL BEHAVIOUR OF SERICIN. III.*

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Sec. VIII. Electro-cataphoresis of the Sericin Solution.

In electro-cataphoresis, an electromotive force acts on an interface, the electric current flowing tangentially to the plane of the interface and causing a movement of a solid with respect to the liquid. Concerning electric properties of sericin particles there has been little work. But, it is long recognized that sericin micellæ possess a negative charge. The charge on protein molecules in solution on either side of the isoelectric point is due to the ionization of protein salts.

Having a light passing through the cataphoretic tube at right angle to the plane of the tube, I measured the migration of the boundary between the sericin sol and the dispersing medium under the influence of electric potential. The cataphoretic velocities of proteins obtained recently by many authors are quoted in Table 46.

Table 46.

Protein	Cataph. velocity	pH	Author
Gelatin	-0.43 ($\frac{\mu}{\text{sec.}}$)	5.4	Mattson, 1932 ⁽²⁴⁾
Egg albumin	-0.35	5.0	Abramson, 1928 ⁽²⁵⁾
„ „	-0.38	5.1	Mattson, 1932
Casein	-1.89	5.2	König, 1932 ⁽²⁶⁾
Serum albumin	-1.11	4.02	„ „
Pseudo-globulin	-2.15	3.73	„ „

* Continued from page 260 of this volume.

(24) Mattson, *Soil Science*, **33** (1932), 43.

(25) Abramson, *J. General Physiol.*, **12** (1929), 711-725.

(26) König, *Biochem. Z.*, **252** (1932), 325-342.

The cataphoretic velocity of the protein solution is much smaller than that of hydrophobic colloids as seen from Table 46.

(1) **The Migration Velocity of Sericin Particles.** In the case of dilute solutions of sericin I added small definite amounts of pumice suspension in order to make the migration of the boundary easily observable. As shown by Abramson and Mattson it appeared that the pumice particles were coated with the protein and behaved electrokinetically as well as the protein, and no difference in cataphoresis was observed on addition of pumice.

A sericin solution (5 c.c.) containing small amounts of pumice suspension was mixed with the same volume of a citric acid phosphate buffer solution and the mixture was put in the cataphoretic tube and the migration velocity was measured after passing an electric current for 15 minutes. The experimental results obtained are shown in Table 47 and Fig. 20.

Table 47.

Variation of cataphoretic velocity with concentration at various pH values.
(For good "kaijo")

pH	Concentration of sericin sol.			
	0.542%	0.50%	0.235%	0.18%
	<i>u</i>	<i>u</i>	<i>u</i>	<i>u</i>
3.6	+0.242	+0.270	+0.383	+0.415
3.8	+0.225	+0.255	+0.355	+0.375
4.0	+0.180	+0.207	+0.277	+0.325
4.2	+0.137	+0.154	+0.230	+0.250
4.4	-0.010	-0.020	-0.060	-0.080
4.6	-0.050	-0.085	-0.119	-0.179
5.0	-0.152	-0.190	-0.306	-0.323

u denotes μ /sec. for 1 volt/cm.

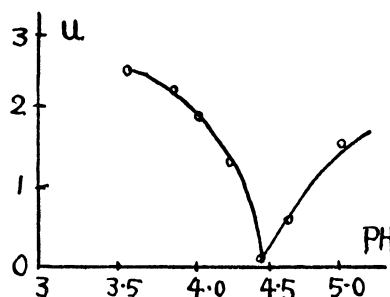


Fig. 20.

Sericin particles prepared by a usual method were transported to the anode in the electric field. The rate of migration, however, is a function of the hydrogen-ion concentration of the solution. It is found that at the isoelectric point there is no charge; on either side of this point there is a charge, positive in acid and negative in alkali, which rises to a maximum till a certain point is reached (Fig. 20). It may be regarded as the result of an increase of charge caused by increased ionization.

At the constant pH value the cataphoretic velocity of sericin particles diminishes gradually with increasing concentration and the speed of migration is greatest for the sericin obtained from the cocoon of good "kaijo" and much slower for that obtained from the cocoon of bad "kaijo"

under the same conditions. With proteins which form molecular aggregates the potential difference between the particle and liquid in which it lies is influenced by the distribution of diffusible ions around the surface of the particle.

The theory of the electrokinetic phenomena was first given by Helmholtz and he assumed a double layer on the interface between the two phases; for cataphoresis he wrote $u = \frac{\zeta HD}{4\pi\eta}$, where u is the cataphoretic velocity of the particle in centimeter per second, ζ the potential of the double layer, H an external potential gradient, D the dielectric constant of water, and η the viscosity of the fluid. We can, therefore, calculate ζ -potential of sericin micellæ from the above formula:

$$\zeta = \frac{4\pi\eta u}{HD}$$

As shown in Fig. 20 the cataphoretic velocity—pH curve is not symmetrical on both sides of the isoelectric point. Isoelectric points obtained from the curves are given in Table 48.

Table 48.

" Kaijo "	pH at isoelec. point
Good	4.35
Middle	4.45
Bad	4.45

(2) **Variation of Cataphoretic Velocity with Temperature.** At low temperature the rate of migration of sericin micellæ is proportional to the temperature which causes a change in the state of aggregation of sericin particles. The results obtained are shown, for example, in Table 49.

Table 49.

For good " kaijo " at pH 3.6.

Temp. <i>t</i> (C.)	Conc. 0.50%		Conc. 0.34%	
	<i>u</i> (μ/sec.)	log <i>u</i>	<i>u</i> (μ/sec.)	log <i>u</i>
0	+0.215	−0.334	+0.236	−0.373
10	+0.225	−0.352	+0.270	−0.431
20	+0.275	−0.439	+0.340	−0.531
30	+0.402	−0.604	+0.502	−0.701
40	+0.750	−0.875	+1.155	−0.062

Logarithm of cataphoretic velocity of sericin micellæ is directly proportional to the temperature in the range between 10° and 40°C., namely,

$$\log u = A + Bt,$$

where t is the temperature in centigrade, and A and B are constants.

(3) **Effect of Electrolytes on the Cataphoretic Velocity.** It is noticed that the rate of migration under the influence of electric potential is proportional to the ζ -potential of particles under the same conditions. When the ζ -potential is changed by the addition of electrolytes, a change in the cataphoretic velocity may be caused. The experimental results are shown in Table 50.

Table 50.

Effect of electrolytes on cataphoretic velocity.
(Conc. of the salt solution = 0.001 mol. pH = 5.0)

Volume (c.c.)	NaCl	KCl	MgCl ₂	CaCl ₂	AlCl ₃	FeCl ₃
	u (0.22%)	u (0.23%)	u (0.24%)	u (0.27%)	u (0.22%)	u (0.22%)
0	-0.31	-0.32	-0.295	-0.285	-0.31	-0.312
0.1	—	—	—	—	-0.04	-0.094
0.2	-0.38	-0.37	-0.25	-0.255	+0.071	+0.037
0.5	-0.46	-0.46	-0.188	-0.209	+0.179	+0.124
0.7	-0.53	-0.52	-0.16	-0.171	+0.160	+0.142
1.0	-0.59	-0.588	-0.156	-0.154	+0.124	+0.122
1.5	-0.581	-0.580	-0.13	-0.120	+0.081	+0.083
2.0	-0.53	-0.48	-0.12	-0.098	+0.069	+0.069

Fig. 21 shows a comparison of salts with cations of different valencies in their influences on the cataphoretic velocity of sericin particles. The abscissa is the volume of salt solutions added, the ordinate the cataphoretic velocity or the ζ -potential. The electrolytes like NaCl and KCl cause the increase of the rate of migration at the low concentrations as is the case with other proteins. AlCl₃ and FeCl₃ change the direction of the cataphoretic velocity in very low

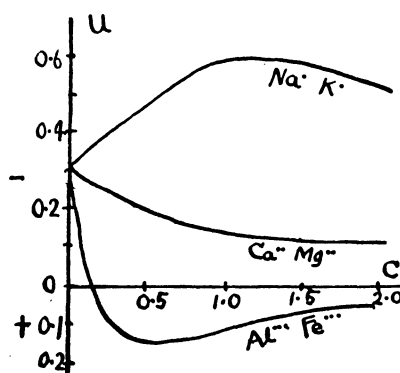


Fig. 21.

concentrations and these salts must be expelled from the water used in the silk industry.

(4) **Effect of Time of Heating on the Cataphoretic Velocity.** When the sericin solution prepared by the usual way is heated again without the cocoon layer in the same flask for a definite time, the viscosity diminishes gradually and at last the capacity of gelatinization is lost. The rate of migration, therefore, is changed by this treatment (Table 51).

Table 51.

Good "kaijo", conc. 0.16% ; pH = 3.8 (20°C.).

Time of heating in hrs. (<i>T</i>)	Cataph. velocity <i>u</i> (μ/sec.)	<i>T</i>	<i>u</i>
0	0.395	2	0.443
0.5	0.406	3	0.450
1	0.410	4	0.490

The cataphoretic velocity of the sericin solution increases with increasing time of heating. This may be due to increase in the degree of dispersion of sericin micellæ and to decrease in the degree of its hydration by further heating.

(5) **Effect of Time of Standing on the Cataphoretic Velocity.** On standing at room temperature the sericin solution gradually gelatinizes, and the effect on the rate of migration may be contrary to that described in (4).

Table 52. (pH = 3.8)

Time of standing (min.)	Good "kaijo "	Bad "kaijo "
	(Conc. 0.306%) Cataph. velocity (μ/sec.)	(Conc. 0.23%) Cataph. velocity (μ/sec.)
0	+0.330	+0.260
60	+0.331	+0.257
120	+0.301	+0.242
180	+0.274	+0.220
240	+0.196	+0.187

As shown in Table 52, the cataphoretic velocity of the sericin solution diminishes with the time of standing. This may be due to increase in the size of aggregates and in the degree of hydration of the sericin micellæ.

Sec. IX. Separation of Sericin into Two Components.

(1) **Separation by Precipitation.** Robin and Verdeil (1853) noticed that magnesium sulphate gave a precipitate with egg-white and with serum. Virchow (1854)⁽²⁷⁾ found further that, besides MgSO_4 , other salts, such as K_2SO_4 , Na_2SO_4 , alum, CaCl_2 , NaCl , possessed the property of precipitating proteins.

Heynsius called attention to the great precipitating power of ammonium sulphate which precipitates albumin from solution. Hofmeister investigated the individual power of the acid- and the metal-groups of the salt to precipitate proteins. His results are quoted in Table 53. The numbers indicate the number of grams in 100 c.c. of solutions when precipitation of globulin commences in a solution of egg albumin.

Table 53.

	Na	K	NH_4	Mg
Sulphate	11.39	No ppt.	13.39	15.93
Acetate	13.83	16.38	No ppt.	No ppt.
Chloride	21.21	26.28	" "	" "
Nitrate	46.10	No ppt.	" "	" "

It is noticed from Table 53 that the capacity of precipitation depends on both the acid- and the metal-groups of a salt. The precipitating power can be arranged in the following order: SO_4 > citrate > tartrate > acetate > chloride > nitrate. This order of the effective influence of the neutral salts has become known as Hofmeister's series.

The precipitation of sericin from solution has been carried out in a variety of ways. Cramer (1965)⁽²⁸⁾ and Wetzel (1898)⁽²⁹⁾ precipitated sericin with lead acetate. Anderlini (1887)⁽³⁰⁾, Türk (1920)⁽³¹⁾, K. Kondo (1921) and T. Watanabe (1928) took advantage of the insolubility of sericin in alcohol.

(27) Virchow, "Über ein eigenthümliches Verhalten albuminöser Flüssigkeiten bei Zusatz von Salzen."

(28) Cramer, *J. prakt. Chem.*, **96** (1865), 76.

(29) Wetzel, *Z. physiol., Chem.*, **26** (1898), 535.

(30) Anderlini, *Chem. Zentr.*, 1887, 941; *ibid.*, 1888, 795.

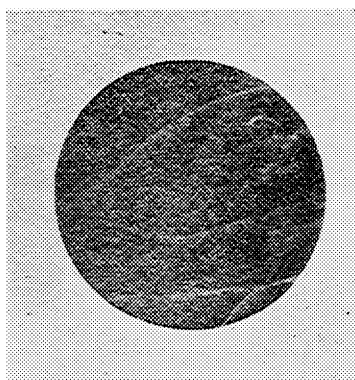
(31) Türk, *Z. physiol. Chem.*, **111** (1920), 69.

I noticed that the sensibility of the sericin solution to the electrolyte is different with "kaijo" of cocoons and that in low concentrations salts do not always precipitate the whole of sericin existing in the solution, but a part of it remains in solution after the addition of salts.

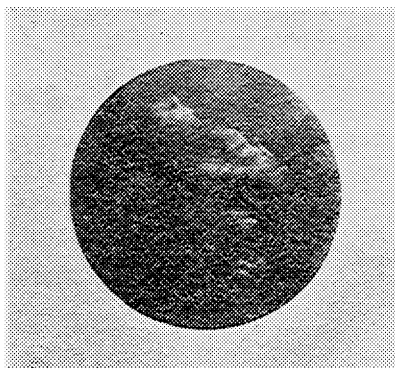
Then it can be considered that sericin must exist in solution in different states of aggregation. So I intended to separate components of sericin by the addition of ammonium sulphate which causes a comparatively slight denaturation of the protein. The application of ammonium sulphate precipitation method to the separation of the sericin components was done by Shelton and Johnson in 1925.⁽³²⁾ They found that varying concentration of ammonium sulphate gave two precipitates; the first of these being a gelatinous substance insoluble in cold water and to obtain it they added ammonium sulphate crystals to the solution.

If a lukewarm sericin solution freshly prepared be one-third saturated with ammonium sulphate, the fibrous precipitation called sericin A is obtained; by half-saturation of the filtrate the amorphous sericin called sericin B can be obtained. In practice, to a lukewarm sericin solution an equal volume of a saturated ammonium sulphate solution is added gradually and the mixture is allowed to stand for some time, sericin A first flocculating on the surface of the solution and then sericin B slowly precipitating from the solution and setting down on the bottom of the vessel.

Sericin A and sericin B precipitated by $(\text{NH}_4)_2\text{SO}_4$



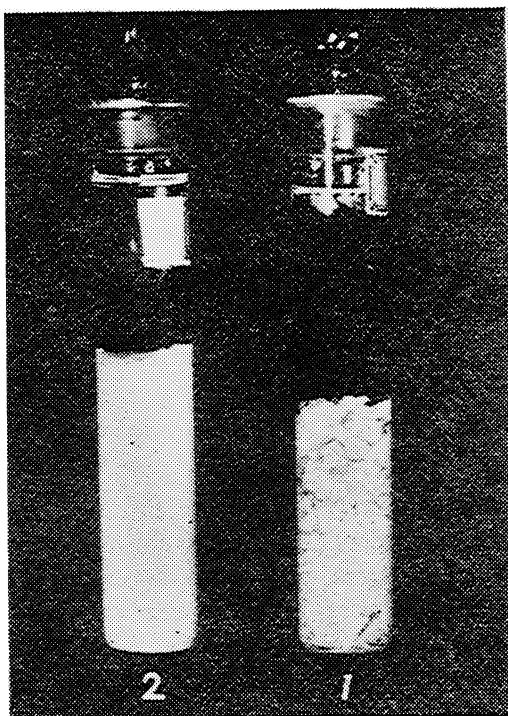
Sericin A ($\times 124$)



Sericin B ($\times 124$)

Fig. 22.

(32) Shelton and Johnson, *J. Am. Chem. Soc.*, **42** (1925), 412-418.



1...Sericin A, 2...Sericin B.

Fig. 23.

The non-spherical colloids, such as casein, fibrinogen or muscle globulin, are more easily precipitated with electrolytes than the spherical. In the case of sericin, sericin A is transparent, elastic, long fibers and easily aggregates together to a mass, but sericin B is white, small granules (Fig. 22 and 23).

After separated from the mother liquor, the precipitate, sericin A and sericin B, was suspended in water and freed from ammonium sulphate by dialysis for a few days and dried slowly over calcium chloride in a desiccator after washing it with alcohol and ether.

Two fractions can be separated from sericin solutions by means of ammonium sulphate, but this separation is difficult for cold or aged sericin solutions.

The proportion of two sericin components is different with "kaijo" of cocoons as shown in Table 54.

Table 54.

	Good "kaijo"	Mid. "kaijo"	Bad "kaijo"
Sericin A : Sericin B	61.97 : 38.03 61.93 : 38.07	55.17 : 44.83 55.27 : 44.73	43.48 : 56.52 43.16 : 56.84
Nitrogen content of sericin A (%)	16.35 } 16.37 } 16.41 16.50 }	16.33 } 16.28 } 16.33 16.39 }	16.25 } 16.40 } 16.33 16.36 }
Nitrogen content of sericin B (%)	16.17 } 16.14 } 16.15 16.14 }	16.07 } 16.10 } 16.10 16.12 }	16.04 } 16.09 } 16.09 16.13 }

Table 54 shows that the sericin solution obtained from cocoons of good "kaijo" contains more sericin A than the solution obtained from cocoons of bad "kaijo," and that the nitrogen content is on an average 16.36 per cent. for sericin A, and 16.11 per cent. for sericin B.

I noticed further that, besides with ammonium sulphate, the separation of sericin into two components can be effected with many other salts and acids. Sericin A is precipitated at low concentrations of precipitating agents, while sericin B remains in solution at such concentrations but is precipitated from the filtrate of A on adding more precipitating agents. In practice, I precipitated sericin B by addition of equal volume of 90 per cent. alcohol after separating sericin A from the solution. For precipitation of sericin A I added aqueous solutions of electrolytes to the sericin solution until the solution remained clear after the precipitation of sericin A.

The nitrogen contents of sericin A and sericin B thus prepared are given in Table 55.

Table 55.

Coagulant	Nitrogen content (%)		Colour of coagulated sericin
	Sericin A	Sericin B	
HgCl ₂	16.42	16.19	Colourless
AlCl ₃	16.37	16.17	"
AuCl ₃	16.47	16.28	Reddish violet
PtCl ₄	16.42	16.18	Slightly yellow
La(NO ₃) ₃	16.38	16.16	Colourless
Er(NO ₃) ₃	16.35	16.17	"
Th(NO ₃) ₄	16.39	16.16	Slightly yellow
Zr(NO ₃) ₄	16.38	16.16	" "
CuSO ₄	16.36	16.15	Slightly blue
Alum	16.38	16.17	Colourless
Uranyl acetate	16.38	16.16	Slightly yellow
HCl	16.40	16.16	Colourless
H ₂ SO ₄	16.40	16.16	"
CCl ₃ CO ₂ H	16.37	16.14	"
(CO ₂ H) ₂	16.40	16.16	"
Phosphotungstic acid	16.37	16.15	Grayish white
Phosphomolybdic acid	16.39	16.15	Grayish blue
Tannic acid	16.35	16.10	Colourless
(NH ₄) ₂ SO ₄	16.36	16.11	

The *pH* of sericin solutions is commonly on the alkaline side of isoelectric point, so sericin forms salts with salts of heavy metals, some of which have a characteristic colour.

The isoelectric point of sericin A and sericin B are respectively *pH* 3.8 and *pH* 4.5. When these two sericins are mixed, the isoelectric point may depend on the proportion of the mixture. The optimal *pH* value for precipitation by electrolytes must be, therefore, varied with "kaijo" of cocoons.

(2) **Separation by the Action of Electric Current.** One hundred c. c. of the sericin solution was subjected to electrodialysis for one hour, whereby a sharp separation of solid sericin A at the anode resulted, leaving a clear liquor containing sericin B, which could be driven out of the solution with alcohol (Table 56).

Table 56.

Nitrogen contents (%) of separated sericins.

" Kaijo "	Sericin A	Sericin B
Good	16.41	16.14
Middle	16.38	16.11
Bad	16.37	16.08

(3) **Separation by Freezing the Sericin Solution.** As it will be described later, two sericins were separated by first gelatinizing the sericin solution at room temperature for two hours and then freezing it. The frozen mass was then melted at 20°C. and filtered through filter paper. The solid residue was sericin A and the filtrate contained sericin B, obtainable in solid form by precipitation with alcohol.

Sec. X. The Precipitability of Sericin on the Action of Reagents.

It has already been mentioned that in dilute solutions salts act as solvents for isoelectric proteins, and that in concentrated solutions near the isoelectric point they act as protein precipitants. The amount needed to initiate precipitation depends on the nature of the added salts. Recent work by Lachs and Chwalinski (1932), showing that in many cases the influence of capillary-active non-electrolytes is to lower the coagulation values of univalent electrolytes and to raise the coagulation value of multivalent ions, is interpreted in terms of charges in the thickness of the electric double layer and the dielectric constant.

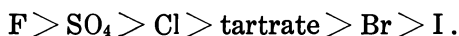
The thickness of the layer is affected only slightly by univalent ions and the dielectric constant then determines the charge in coagulation value, but multivalent ions have a strong influence on the thickness of the double layer. Krulyt and de Jong (1922)⁽³³⁾ have developed a general theory of charge and hydration as dual stability factors, which enables both hydrophilic and hydrophobic sols to be considered from the same point of view. They have shown that when the charge on the particles of an agar hydrosol is removed by electrolytes the sol remains stable, but the sol is flocculated if it also contains a dehydrating substance, such as alcohol or acetone.

Then a hydrophilic sol can be converted into a hydrophobic sol by adding alcohol or acetone and the resulting system can then be precipitated by small quantities of electrolytes.

These phenomena can be also seen in the sericin hydrosol. The molecules of the water of hydration are believed to be oriented around the particle in such a way that the first layers are firmly attached, whilst succeeding layers are less oriented and less firmly attached. The outer layers of less oriented water molecules are removed by dehydration at the iso-electric point.

The precipitation of proteins from solutions by the salts of the Hofmeister series is attributed to the so-called lyophilic action. The action of electrolytes on the hydrophilic colloids is generally very complex and depends upon the valency of cation of the salts, effect of anion, degree of hydration of the protein, and its adsorption capacity, etc.. To some extent Hofmeister's lyotropic series holds good for it.

Gortner⁽³⁴⁾ found that Hofmeister's series exists for the precipitation of wheat flour and that hydrogen- and hydroxyl-ions are adsorped on the surface of protein colloids. The effects of anions are as follows :



With regard to the precipitation of proteins by salts of heavy metals, T. Geill (1929)⁽³⁵⁾ observed that there was generally two precipitation ranges, one in very weak concentration (about 10^{-4} N), and the other in strong concentration (about 1 N).

I found also that there was two precipitation ranges for sericin when the electrolytes, such as $Th(NO_3)_4$, $FeCl_3$, $AlCl_3$, and lead acetate, were added to the sericin solution. The experimental results obtained are given in Table 57.

(33) Krulyt and de Jong, *Z. physik. Chem.*, **100** (1922), 250.

(34) R. A. Gortner, *Kolloid-Z.*, **44** (1928), 97.

(35) T. Geill, *Biochem. Z.*, **216** (1929), 165-178.

Table 57.

Flocculation of sericin with $\text{Th}(\text{NO}_3)_4$.
Conc. of sericin solution = 0.37%

Flocculation of
sericin with FeCl_3 .

Conc. of electrolyte (mol.)	X c.c.	Flocculation	Conc. of electrolyte (mol.)	X c.c.	Flocculation
0.01	0.04	— (no flocc.)	0.01	0.3	—
"	0.07	—	"	0.4	++
"	0.11	+ (slight flocc.)	"	0.7	+++
"	0.14	++ (flocc.)	"	0.1	+++
"	0.16	+++ (most flocc.)	"	0.5	++
"	0.20	++ (flocc.)	"	0.6	—
"	0.30	+	"	5.0	+
"	0.50	—	"	0.20	+++
0.1	0.15	+			+++
"	0.17	++			
"	0.20	+++			
		+++			

X denotes the volume of the electrolyte added to 5 c.c. of the sericin solution.

Pauli⁽³⁶⁾ considered that the precipitation occurring in very weak concentrations of salts of heavy metals was due to the formation of a complex salt of the protein with the cation of a salt, and that in strong concentrations it was due to the formation of a complex salt of the protein with the anion.

Silbermann states in his book, "Die Seide, II", that the aqueous solution of sericin is precipitated by alcohol, ether, metallic salts, and tannin, but not by potassium ferrocyanide nor acetic acid. At 20°C. I measured the flocculation values of the sericin solution, namely the concentrations of electrolytes in solution in millimoles per litre when the sericin is precipitated completely in two hours.

The influence of the nature of the electrolytes, as shown by H. Freundlich⁽³⁷⁾, proves that we are dealing with an electric phenomenon. The ions which are the most effective are those having a charge opposite in sign to that of the colloidal particles and the adsorbility and valency of these ions are of great importance.

(36) Pauli, *Biochem. Z.*, **233** (1931), 87-112.

(37) Freundlich, *Z. physik. Chem.*, **114** (1924), 65.

(1) **Flocculation Values for the 0.2 per cent. Sericin Solution.** As already shown, the sericin sol possesses a negative charge like arsenic trisulphide sol, so the cations of salts must influence remarkably the flocculation values for sericin sol. Table 58 gives the flocculation values for sericin sol.

Table 58.

Flocculation value r for 0.2% solution.

Cation	Salt	r	Salt	r	Salt	r
Mono-valent	AgNO ₃	12.28	C ₆ H ₅ NH ₂ ·HCl	2.84		
Bi-valent	HgCl ₂	6.53	Zn(NO ₃) ₂	5.66	CuCl ₂	3.84
	(CH ₃ CO ₂) ₂ Cu	1.07	(CH ₃ CO ₂) ₂ UO ₂	1.07	Cu(NO ₃) ₂	1.07
	CuSO ₄	0.91				
Trivalent	FeCl ₃	0.740	[Co(NH ₃) ₆]Cl ₃	0.740	(CH ₃ CO ₂) ₃ Fe	0.740
	AlCl ₃	0.570	Al(NO ₃) ₃	0.566	La(NO ₃) ₃	0.566
	Fe(NO ₃) ₃	0.384	Er(NO ₃) ₃	0.360	$\frac{1}{2}$ Al ₂ (SO ₄) ₃	0.470
Tetra-valent	Zr(NO ₃) ₄	0.384	Th(NO ₃) ₄	0.196		
Acids	HCl	1.57	H ₂ SO ₄	0.785	(CO ₂ H) ₂	0.590
Alkaloidal reagents	Tannin	37.03	CCl ₃ CO ₂ H	0.740	Lead acetate	0.384
	P. T. acid	0.122	P. M. acid	0.566		

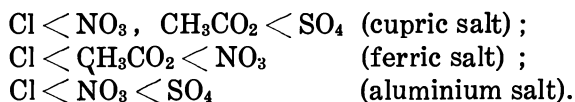
P. T. acid = phosphotungstic acid. P. M. acid = phosphomolybdic acid.

(2) **Flocculation Values for the 0.4 per cent. Solution.**

Table 59.

Cation	Salt	r	Salt	r	Salt	r
Mono-valent	AgNO ₃	13.79	C ₆ H ₅ NH ₂ ·HCl	3.84		
Bi-valent	HgCl ₂	7.40	Zn(NO ₃) ₂	7.40	CuCl ₂	5.66
	(CH ₃ CO ₂) ₂ Cu	1.37	Cu(NO ₃) ₂	1.379	(CH ₃ CO ₂) ₂ UO ₂	1.228
Trivalent	La(NO ₃) ₃	1.66	FeCl ₃	1.071	[Co(NH ₃) ₆]Cl ₃	0.91
	AlCl ₃	0.740	Al(NO ₃) ₃	0.740	(CH ₃ CO ₂) ₃ Fe	0.740
	Fe(NO ₃) ₃	0.566	$\frac{1}{2}$ Al ₂ (SO ₄) ₃	0.940	Er(NO ₃) ₃	0.91
Tetra-valent	Zr(NO ₃) ₄	0.91	Th(NO ₃) ₄	0.31		
Acids	HCl	1.96	H ₂ SO ₄	1.20	(CO ₂ H) ₂	1.07
Alkaloidal reagents	Tannin	74.07	CCl ₃ CO ₂ H	0.91	Picric acid	2.06
	P. M. acid	0.384	Lead acetate	0.375		

From the figures, we find the following facts. Sericin sol is negatively charged; the added anion, which also has a negative charge, apparently plays a subordinate rôle in the flocculation process. On the other hand, the valence of the cation governs, to a great extent, the flocculating power of the added electrolyte. It is noticed that HgCl_2 and $\text{Zn}(\text{NO}_3)_2$ give flocculation values about 6.0 milli-moles, while aluminium, iron, and lanthanum give values in the neighborhood of 0.6 milli-mole. The hydrogen-ion and ions of heavy metals have a greater flocculating power than is expected from their valences. But, the salts having cations of the same valence do not show the same flocculation value. The effects of anions are in the order given below :



It can be seen that Hofmeister's series holds goods here.

(3) **Flocculation Value and Concentration of Sol.** When I investigated the flocculation values for sericin sols of different concentrations, the following results were obtained.

Fig. 24 shows that dilution of the sol lowers the flocculation values of many salts. Like the case of the adsorption formula, the logarithm of flocculation value is a linear function of the logarithm of the concentration of sericin sol (Fig. 25).

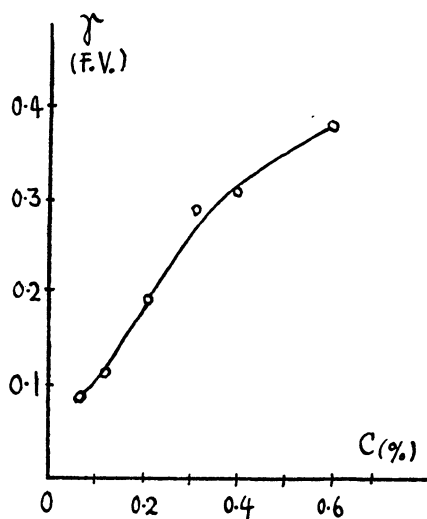


Fig. 24.

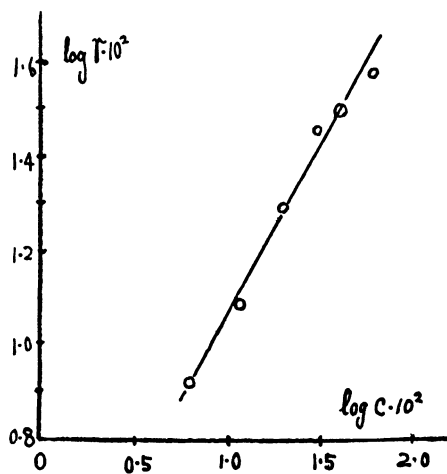


Fig. 25.

$$r = k \cdot c^{\frac{1}{n}} \quad \text{or} \quad \log r = \log k + \frac{1}{n} \log c$$

(4) **Flocculation value and pH value.** Sericin has a wide coagulation range in pH values, for it is a mixture of at least two components. And the coagulation range is varied slightly with electrolytes (Table 60).

Table 60.

	Floc. range (pH)	Optimal floc. (pH)
(a) Acid (HCl, H ₂ SO ₄)	3.5-4.4	3.9
(b) Salt (FeCl ₃ , AlCl ₃ , CuSO ₄)	3.6-4.6	4.2
Salt (nitrate)	3.8-4.8	4.6

In the presence of citric acid-phosphate buffer solution, the coagulation range is extended to more acid side and the optimal coagulation point exists near pH 4.0.

(5) **Flocculation of Sericin with Alcohols and Acetone.** As already shown, not only proteins are held in solution by their electric potential, but also their stability is influenced by association with water. Even electrically charged proteins can in some cases be driven out of solution by substances, such as alcohols and acetone, which have the power of extracting this water from the particles. Sericin is, therefore, precipitated from solution by addition of alcohols and acetone. The two constituents of sericin are precipitated by different concentrations of an alcohol. With increasing disaggregation of the micellæ, the precipitability by alcohols decreases so that a fractionation of sericin is possible on the basis of their alcoholic solutions as done by T. Watanabe.⁽³⁸⁾

When the dielectric property of the sericin solution is changed by addition of some organic substances, like chloroform, carbon tetrachloride, benzene, and aniline, sericin is also flocculated from solution.

(a) **Alcohols.** Ethyl alcohol in 80 per cent. concentration precipitates sericin from solution and the pH value of the maximum precipitability is varied in the presence of other substances. The optimal pH values for precipitation of dialysed sericin by ethyl alcohol are as follows:

(38) T. Watanabe, loc. cit.

- pH 4.50 (+ 0);
 pH 3.8–3.9 (+ citric acid-phosphate buffer solution);
 pH 3.75 (+ small amount of ammonia);
 pH 4.60 (+ small amount of CO_2).

One c.c. of an alcohol was added to the mixture of 2 c.c. of the sericin solution (0.41%) and 3 c.c. of the buffer solution and the mixture was shaken thoroughly. After two hours' standing at room temperature the optimal pH values for precipitation of sericin was determined, which are shown in Table 61.

Table 61.

Alcohol	Opt. flocc. (pH)	Alcohol	Opt. flocc. (pH)
CH_3OH (85%)	4.0	C_4H_9OH (iso.)	4.2
C_2H_5OH (95%)	3.8	$C_5H_{11}OH$	4.4
C_3H_7OH (90%)	3.6		

The flocculation power of alcohols decreases with increasing dilution of them and at the same time the pH value of the maximum precipitability is shifted to the more acid side.

Jirgensons (1931)⁽³⁹⁾ showed that the coagulating influence of phenol, acetone, and certain alcohols on hydrosols of starch or egg-albumin rose with increasing concentration, attaining a maximum at a certain concentration which is a linear function of the dielectric constant of the coagulants. On adding an alcohol to the discharged sericin sol to which a minute quantity of an electrolyte had been added, an immediate flocculation occurred.

The precipitability of sericin sol by alcohols was sensitized by addition of minute quantities of $AlCl_3$ (0.0001–0.005 mol.). $FeCl_3$ had also a sensitizing effect at very weak concentrations (0.0001–0.005 mol.), but a stabilizing effect at strong solutions (0.01–0.4 mol.). Glycocoll (0.0008 mol.) and ammonium oxalate (0.005–0.1 mol.) acted as stabilizer in the flocculation of sericin by alcohols.

(b) **Acetone.** Acetone had a similar action on the sericin solution. In the low concentrations sericin A was apt to flocculate easily with acetone, for its isoelectric point lies near pH 3.7.

(39) B. Jirgensons, *Biochem. Z.*, **240** (1931), 218–231.

Table 62.

(2 c.c. Sericin solution + 3 c.c. Buffer solution + 1 c.c. Acetone).

Conc. of acetone (Merck) (%)	Opt. floc. (pH)	Floc. range (pH)	Precipitate
100	4.0	3.6-4.8	Floats, voluminous
83	3.8	3.6-4.2	Large form
50	3.6	3.4-3.8	Small form
33	3.6	3.4-3.8	" "
10	3.6	3.4-3.7	" "

The change in the concentration of acetone caused also the variation in the pH value of the maximum precipitability of sericin. Most of the aging phenomena of sols are in general characterized by the fact that the particles of a highly dispersed solution gather to form larger particles, and that their sensitiveness to flocculation is increased.

(6) **Form of Coagulated Sericin.** When electrolytes, such as thorium nitrate, zirconium nitrate, ammonium sulphate, mercuric chloride, phosphomolybdic acid, and uranyl acetate, were added to the sericin solution, the long, fibrous precipitates were obtained, which are illustrated in Fig. 26.

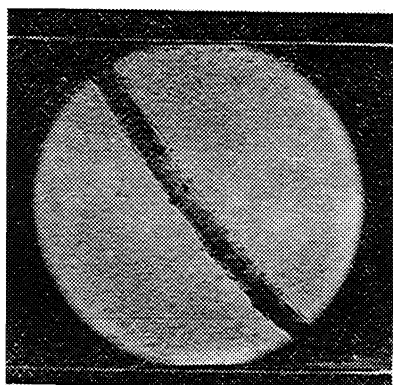
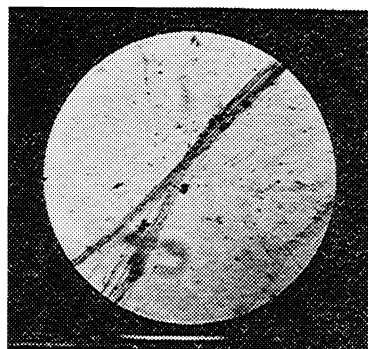
A. $(\text{NH}_4)_2\text{SO}_4$ B. HgCl_2

Fig. 26.

Especially sericin A gave easily a fibrous coagulant which had elasticity and shrank to mass on stirring. It can be, therefore, considered that

sericin A has a micellar structure like fibroin, and sericin B an amorphous structure. By the optical method K. Obara (1932)⁽⁴⁰⁾ showed that sericin coating the silk fiber might have also a micellar structure. Then the high viscosity of sericin A may be explained by this consideration. On freezing the solution, sericin precipitated also in the form of fiber.

Sec. XI. The Distribution of Sericin Particles in the Electric Field.

If the particles combine with alkali, they would migrate to the anode, and if with acid, to the cathode. I observed the behaviour of sericin particles in Burton's cataphoretic apparatus. Towards the end of five minutes of passing the electric current under 110 volts, a white thin coagulant was produced near the boundary between sericin sol and water layer at the anodic side. The sericin solution in the anodic side gradually became more turbid and that in the opposite side was tinged with slight yellowish colour.

The anodic layers were acidic, the cathodic alkaline as in the case of the cocoon layer used as the diaphragm in distilled water. The sericin layer obtained from the cocoons of bad "kaijo" showed deeper yellow colour in the cathodic side.

(1) **Reactions of Each Liquid Layer.** Sericin particles in the cathodic side were easily coagulated with copper sulphate or lead acetate, but those in the anodic side were not flocculated with them, though both were precipitated with alcohol or ammonium sulphate.

Though the change of colour in the biuret reaction depends on the concentration of the sericin solution, sericin in the anodic side gave always a more intense tinge of red than that in the cathodic side. Then we can presume the degree of "kaijo" of cocoons from the colour reaction of the anodic layer. The relation between biuret reaction and the concentration of sericin are shown in Table 63.

Table 63. (Good "kaijo").

Conc. (%)	Anodic side		Cathodic side	
	Sericin layer	Water layer	Sericin layer	Water layer
Above 0.35	Brownish red	Violet	Violet red	Slightly blue violet
0.35-0.25	Pink	Slightly violet	Violet red	—Colourless Colourless

(40) K. Obara, *Bull. Inst. Phys. Chem. Research, Japan*, **11** (1932), 466.

Table 63.—(Concluded)

Conc. (%)	Anodic side		Cathodic side	
	Sericin layer	Water layer	Sericin layer	Water layer
0.25–0.15	Violet red	Slightly violet	Red violet	Colourless
0.15–0.05	Red violet	Slightly blue violet	Violet	„
Below 0.05	Red violet	Colourless	Violet	„

The change of the colour of the biuret reaction depends not only on the concentration of sericin, but also on other soluble matters which exist with sericin in the cocoon fiber and become free in the electric field.

(2) **Isoelectric Point of Sericin Solutions in Cathodic and Anodic Sides.** The isoelectric point was measured by the change of surface tension. For the anodic sericin solutions the isoelectric point existed nearly at pH 3.80 and for the cathodic sericin at pH 4.40, although they had considerably different “kaijo” (Table 64).

Table 64.

“ Kaijo ”	pH at isoelectric point	
	Anodic sericin	Cathodic sericin
Very good	3.70	4.36
Common	3.80	4.45
Bad	4.00	4.50

(3) **The Nitrogen Contents of Sericin in Both Solutions.** Though the amounts of sericin existing in both sides varied with the “kaijo” of cocoons, the nitrogen contents of sericin in the solutions were nearly equal and were found on an average 16.15 per cent. for sericin in the anodic solution and 16.01 per cent. for sericin in the cathodic solution (Table 65).

Table 65.

“ Kaijo ”	N (%) anodic	N (%) cathodic
Good	16.156	16.08
Common	16.156	16.01
Bad	16.143	16.01

From the nitrogen content it can be considered that the anodic sericin is rich in sericin A and the cathodic in sericin B. The outer, middle, and inner layers of cocoons have different "kaijo", but their anodic and cathodic sericins showed nearly the same nitrogen contents as described above. Both sericin solutions were also found already in the liquid silk in the silkworm. It is, therefore, clearly understood that the "kaijo" of cocoons is ascribed first to the varieties of the silk worm, secondly to the physiological values of mulberry leaves and the external effects on the gelatinization of liquid silk.

(To be continued.)

ON THE CRACKING OF POLYCYCLIC COMPOUNDS.

By Shozo YAMAGUCHI.

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When an organic compound is subjected to heat, the rise in the temperature of the molecule due to the increase of its vibratory energy, finally decomposes it into simpler molecules. Such a cracking of organic compounds is considered to occur by breaking a link between two certain atoms somewhere in the molecule, since the bonds in it are not all of the same strength.

The evidence so far studied has shown that in a cracking of a higher paraffin hydrocarbon, the rupture of a link of a C-C bond results in forming one or more molecules of an olefine hydrocarbon as a primary dissociation of the molecule; and in case of unsaturated hydrocarbons, the C=C bond, being approximately twice as strong as the C-C bond, will remain without rupture in the molecule.⁽¹⁾

In monocyclic compounds, such as benzene and cyclohexane, the inner energy of the molecule being distributed equally to all the carbon atoms composing the ring, the cracking of the ring compound is entirely different from the open chain compounds as indicated in the experiments on both compounds by R. Conrad and his co-workers.⁽²⁾

The study of the thermal decomposition of polycyclic compounds will not only afford evidence for the energy distribution in the molecule, but also may add some important contribution to a theory for production of gasoline from heavy oily substances such as coal tars or petroleum. The present study, therefore, deals with naphthalene, quinoline, and isoquinoline of bicyclic compounds, and tricyclic anthracene, as they occur in petroleum and other tar products.

Although naphthalene is usually represented by a bicyclic formula consisting of two condensed benzene nuclei, on reduction with hydrogen and

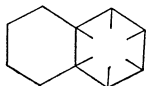


Fig. 1.

nickel catalyst it is transformed into tetraline. Its dipole nature being 0.7, the chemical and physical natures of naphthalene are represented by the structural formula of C. Harries and R. Willstätter⁽³⁾, which has two different carbon rings, Fig. 1.

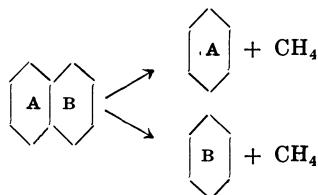
(1) F. O. Rice, "Free Radicals," 1933, p. 152; A. E. Dunstan, E. N. Hague, and R. V. Wheeler, *J. Soc. Chem. Ind.*, **50** (1931), 313; H. Gault and Y. Altchidjiam, *Compt. rend.*, **178** (1924), 2092; and also refer G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," 1932, p. 105.

(2) *Z. Elektrochem.*, **36** (1930), 654; "Free Radicals," 1933, p. 215.

(3) R. Müller, *Samm. Chem. u. Chem. Tech. Vorträge*, **30** (1928), 1.

The theory that naphthalene molecule is represented by a formula consisting of two benzene nuclei considered unequal in view of energy distribution, is advocated by Dr. S. Kimura in his study of hydronaphthalenes.⁽⁴⁾ According to this hypothesis, on cracking, naphthalene will yield derivatives of benzene by disruption of the more unstable one of the two rings.

When naphthalene is heated in an autoclave under high pressure of hydrogen, the dissociation of the polycyclic compound into monocyclic free radicals may occur in one of two ways according to the stability of the rings :



The free radicals thus formed usually undergo secondary reaction to form complicated products. In order to minimize, if possible, the subsequent course of reaction of the free radicals produced in the primary decomposition, and also to intensify the cracking by the heat transfer, hydrogen under high pressure is used ; this will saturate the free valence of the fragments before polymerisation can occur. When naphthalene (100 g.) was heated at 500° for 5 hours in the presence of calcium chloride with hydrogen of 80 atmospheric pressures at 0°, 60 per cent. of the substance was cracked and the reaction product was found to consist of liquid and gaseous substances. The former consists of benzene and its homologues and the latter of methane and ethane, and their percentages in the product are given in Table 1.

The theoretical yields of methane in mols with the formation of 1 mol benzene or its homologues from 1 mol of naphthalene are as follows :

Table 1.

Substance	Yield	No. of mols from 1 mol of naphthalene
Benzene	4.8 g.	0.08
Toluene	14.1 „	0.20
Xylene	18.0 „	0.22
Methane	4.8 „	0.40
Ethane	19.8 „	0.46

With benzene 4 mols methane

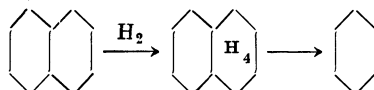
„ toluene 3 „ „

„ xylene 2 „ „

The actual yield of the gaseous hydrocarbons calculated as methane is 1.3 mols, which agrees with 1.36 mols of methane calculated from molar yield of benzene and its homologues based on

(4) *Mem. Coll. Sci. Kyoto Imp. Univ.*, A, **14** (1931), 307.

the theory shown above. The cracking of naphthalene under high pressure of hydrogen, therefore, may be represented by the following scheme when we take M. A. Sundgren's⁽⁵⁾ experiment on hydronaphthalene into consideration:



The cracking of anthracene was performed under the same conditions, and the compound was perfectly decomposed into 20 per cent. gaseous hydrocarbons such as methane and ethane, and 80 per cent. other hydrocarbons. The latter contained 47 per cent. naphthalene and its derivatives, 27 per cent. benzene and its homologues, and 10 per cent. dianthracene; the molar yield of benzene and its homologues is almost equal to that of naphthalene and its homologues. This fact indicates that two decomposition reactions occur simultaneously but with different velocities, namely the rupture of the B-ring and one of two A-rings (Table 2):

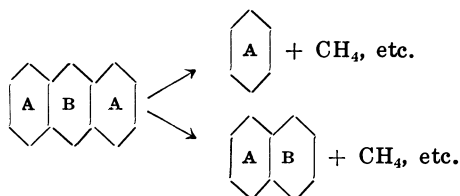


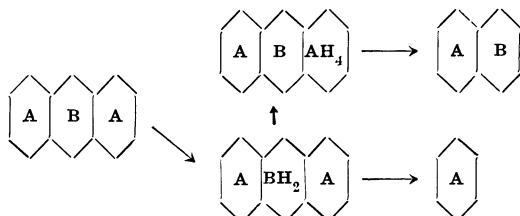
Table 2.

	Yield			
Benzene	6.4 g.	0.146 mol	} 0.55 mol	
Toluene	14.3 „	0.295 „		
Xylene	6.2 „	0.113 „		
Naphthalene	15.8 „	0.220 „	} 0.58 „	
Dimethyl-naphthalene	31.3 „	0.357 „		
Dianthracene	10.1 „	0.050 „		0.05 „
Methane	3.6 „	0.401 „	} 1.37 „	
Ethane	16.3 „	0.967 „		

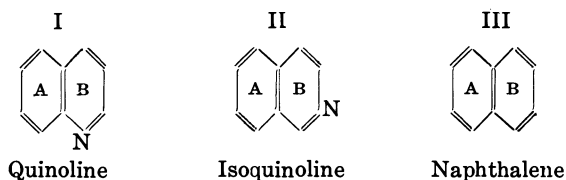
The hydrogenation of anthracene in the presence of a catalyst proceeds by adding the first two hydrogen-atoms to the B-ring, and the dihydro-compound thus formed will be instantly transformed into tetrahydro-com-

(5) "La décomposition pyrogénée du tétranaphtalène et du décanaphtalène." *Ann. Combustibles Liquides*, **5** (1930), 35; and refer Ipatiew and Orlov, *Ber.*, **60** (1927), 1950; **62** (1929), 711, 719, 1226; **63** (1930), 2179.

pound. Thus, cracking of anthracene under pressure of hydrogen produces dihydro-anthracene, which partly decomposes into benzene homologues and is partly converted into tetrahydro-anthracene. This in turn is cracked into naphthalene derivatives.

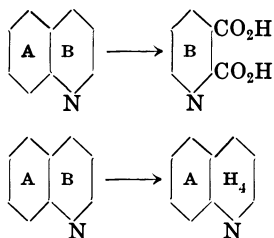


Quinoline and isoquinoline, which are bicyclic compounds, are formulated in the same way as naphthalene in which an α - or β -CH-group is replaced by N.



Benzene nucleus A and pyridine nucleus B in the formulas I and II may evidently differ from each other in the energy content, since the heats of combustion of benzene and of pyridine are 787 cal. and 660 cal. respectively.

Such an assumption of the energy content of ring systems agrees with the fact that quinoline, when oxidized with potassium permanganate, opens the benzene nucleus with production of quinolinic acid, and that when quinoline is reduced with sodium and alcohol it takes up four atoms of hydrogen, forming tetrahydro-quinoline, the hydrogen atoms adding almost exclusively to the pyridine ring. The same phenomena occur of course in the case of naphthalene.



From these facts it is evident that when quinoline is cracked under high pressure of hydrogen at 450°, the pyridine nucleus in the quinoline molecule is reduced. The tetrahydro-compound so formed undergoes de-

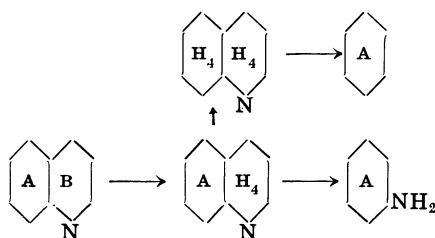
composition into benzene homologues or aniline derivatives, as naphthalene gives benzene homologues. As a matter of fact, when quinoline (50 g.) was heated at 450° for 4 hours with hydrogen of 80 atmospheric pressures at 0°, 90 per cent. of the substance was decomposed and 50 per cent. was composed of aniline and its homologues including methyl-indole; in other words, 1 mol of quinoline gave on cracking 0.5 mol of aniline-derivatives, 0.16 mol of hydrocarbons of cyclohexane and benzene homologues, and 0.21 mol of ammonia and amines (Table 3).

Table 3.

	Yield		
Aniline	2.7 g.	0.04 mol	0.5 mol
<i>o</i> -Toluidine	14.5 „	0.18 „	
<i>o</i> -Ethyltoluidine	5.6 „	0.06 „	
<i>o</i> -Propyltoluidine	3.5 „	0.03 „	
Methyl- <i>o</i> -toluidine	1.6 „	0.02 „	
Ethyl- <i>o</i> -toluidine	1.2 „	0.03 „	
Methyl-indole	15.4 „	0.16 „	
Cyclohexane	2.0 „	0.03 „	0.16 „
Methylcyclohexane	1.4 „	0.03 „	
Ethylcyclohexane	1.7 „	0.03 „	
Propylcyclohexane	3.6 „	0.04 „	
Toluene	0.5 „	0.007 „	
Ethyl-benzene	0.5 „	0.006 „	0.21 „
Propyl-benzene	0.5 „	0.004 „	
Ammonia	1.37 „	0.21 „	
Methane	2.70 „	0.44 „	0.70 „
Ethane	3.00 „	0.26 „	

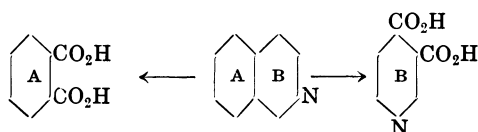
The experimental results resemble those gained from the experiments on the cracking of hydroquinoline by Padoa and his co-workers.⁽⁶⁾

The cracking of quinoline, therefore, will be represented by the following scheme in which hydroquinoline is supposed to be formed during the process of cracking.



(6) Padoa, Carughi, and Seagliarini, *Chem. Zentr.*, 1906, II, 1011; 1908, II, 114.

To our astonishment, no traces of pyridine and its homologues are present in the cracking product of quinoline. Then it follows that benzene and pyridine nuclei in the quinoline molecule are not equivalent in energy content. Such a consideration on the bicyclic compound may be applied to isoquinoline in which benzene and pyridine nuclei occur as in the quinoline molecule. However, the structural difference is evidently manifested in the result of oxidation with potassium permanganate; quinolinic acid is formed from quinoline, while phthalic acid and cinchomeric acid are formed from isoquinoline :



Thus the stability of the pyridine ring is greater in isoquinoline than in quinoline.

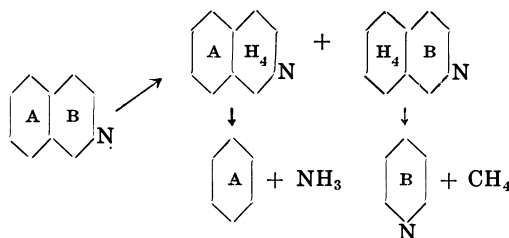
In fact, the cracking of isoquinoline at 450° gives 5 per cent. pyridine and its homologues, 38 per cent. toluene and other aromatic hydrocarbons, about 10 per cent. of unchanged material, and 9 per cent. gaseous products.

The molar yields of the cracked substances are 0.06 mol pyridine bases, 0.4 mol aromatic hydrocarbons, and 0.65 mol gaseous bases (Table 4).

Table 4.

	Yield			
Pyridine	1.3 g.	0.03 mol	}	0.1 mol
Methyl-pyridine	1.6 „	0.03 „		
Dimethyl-pyridine	1.9 „	0.03 „		
Toluene	4.3 „	0.06 „	}	0.4 „
o-Xylene	12.6 „	0.15 „		
Indane	18.5 „	0.20 „		
Dimethyl-anthracene	2.3 „	0.01 „	}	0.65 „
Ammonia	4.3 „	0.65 „		
Methane	2.7 „	0.43 „		
Ethane	2.2 „	0.18 „	}	0.61 „

The writer, therefore, suggests the following reactions in the cracking of isoquinoline as the most probable :



In conclusion, in the cracking of polycyclic compounds under high pressure of hydrogen, the more reactive ring takes first hydrogen atoms and the hydrogenated ring breaks before the other. There exists an optimum temperature for cracking which depends upon the chemical nature of substances; above this temperature the dehydrogenation becomes predominant. The manner of the ring rupture of the polycyclic compounds would be foreseen from their behaviour in catalytic reduction or in other words from the study of the energy content of ring systems.

Experimental.

The naphthalene, anthracene, quinoline, and isoquinoline used in the experiments were all proved to be fairly pure by their physical constants as shown in Table 5.

Table 5.

	B. p.	M. p.	n_D^{25}	d^{25}
Naphthalene	215-218	81°	—	—
Anthracene	—	216°	—	—
Quinoline	235-238°	—	1.6238	1.0894
Isoquinoline	238-240°	—	1.6239	1.0984

In the experiment, a weighed sample was introduced into an autoclave, and after the air in it was replaced by hydrogen, and the hydrogen gas was raised to the required pressure, it was heated externally to the required temperature by an electrical resistance furnace.

During the reaction, the autoclave was shaken by a machine to bring the substances in agitated state, and changes of temperature and pressure during the reaction were recorded every ten minutes.

After the reaction the apparatus was cooled. The volume of gas in it was measured, and the chemical composition and physical properties of the gas and of other reaction products were examined carefully.

(1). **Naphthalene.** When naphthalene (100 g.) was heated for 6 hours with a small amount of calcium chloride at 500° with hydrogen of 71 atmospheres at 0°, a fall of 11 atmospheric pressures was observed.

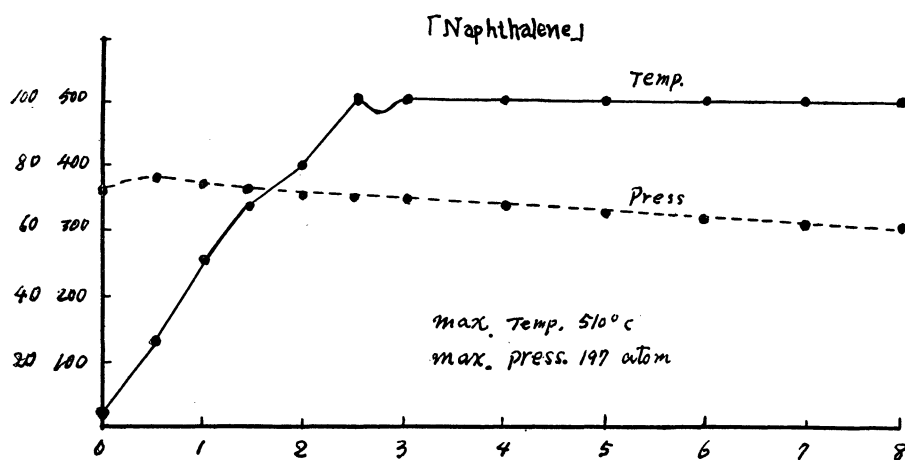


Fig. 2.

The gas in the autoclave was determined to be composed of 84.9 per cent. of H_2 , 10.3 per cent. of C_2H_6 , 4.6 per cent. of CH_4 , and 0.2 per cent. of C_nH_m . The reaction product (67 g.) in the autoclave consisted of liquid and solid substances, which were separated by filtration. The solid substance separated from the liquid amounted to 10 g. and was found to be naphthalene, for, after it was purified by recrystallization from alcohol, it melted at 81°, and its picrate at 151°. The liquid reaction product (65 g.) was subjected to fractional distillation under 759.5 mm. pressure over metallic sodium and separated into six fractions with the physical constants shown in Table 6.

Table 6.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	75-90	4.5	1.497	0.869	Benzene
2	90-120	13.1	1.496	0.867	Toluene
3	120-140	10.1	1.495	0.865	Ethyl-benzene
4	140-155	3.0	1.499	0.871	<i>o</i> -Xylene
5	155-200	4.8	1.531	0.916	
6	200-220	26.5	Solid		

The fractions 1 and 2, as indicated by their physical constants, were assumed to be composed of benzene and toluene respectively; the former was confirmed by changing it into nitrobenzene and then reducing it to aniline, and the latter was oxidized to benzoic acid (m.p. 121°) by potassium permanganate.

The fractions 3 and 4 were supposed from their physical constants to be a mixture of *o*-xylene and ethyl-benzene.

The fraction 5, consisting of naphthalene, xylene, and ethyl-benzene, was treated with picric acid in an alcoholic solution in order to separate naphthalene. The picrate separated from volatile hydrocarbons by distillation under reduced pressure amounted to 4.8 g., from which pure naphthalene was isolated in a yield of 1.2 g. The mixture of hydrocarbons separated from naphthalene weighed 3.6 g., and from its boiling point $124-145^{\circ}$, refractive index $n_D^{25} = 1.4981$, and density $d_4^{25} = 0.8695$, the proportion of xylene and ethyl-benzene was calculated to be about 7:3. Fraction 3 was composed of naphthalene as shown by the physical properties and also by the formation of the picrate.

(2) **Anthracene.** Anthracene (100 g.) was heated at 500° for 6 hours with 10 g. of calcium chloride and hydrogen of 84 atmospheric pressures at 0° . The fall in the pressure was 17.6 atmospheres at 0° . The gaseous product was composed of 89.1 per cent. of H_2 , 3.2 per cent. of CH_4 , 7.6 per cent. of C_2H_6 , and 0.1 per cent. of C_nH_m . From the reaction product 10 g. of solid and 74 g. of liquid ($d_4^{25} = 0.984$, $n_D^{25} = 1.584$) were isolated.

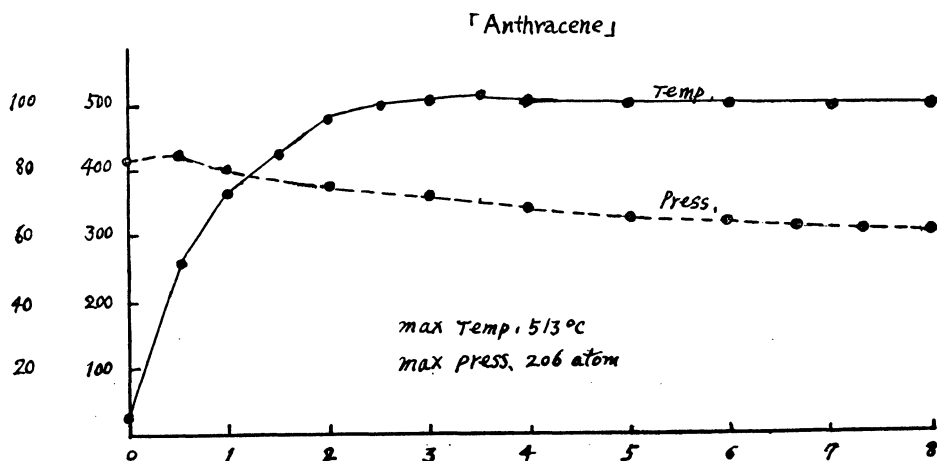


Fig. 3.

The liquid reaction product (70 g.) was fractionated over metallic sodium as shown in Table 7.

Table 7.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	75-90	6.0	1.490	0.858	Benzene
2	90-120	13.5	1.495	0.862	Toluene
3	120-140	1.5	1.497	0.866	Ethyl-benzene
4	140-200	3.2	1.528	0.895	<i>o</i> -Xylene
5	200-220	8.7	Liquid with crystals		Naphthalene
6	220-240	13.5			
7	240-270	13.5	Resin with crystals		
8	270-350	5.0			
9	Residue	5.1			

The fractions 1 and 2 were identified by their physical and chemical properties with benzene and toluene respectively; and the fractions 3 and 4 were assumed to be mixtures of xylene and ethyl-benzene from their physical constants.

Fractions 5 and 6, containing some crystals which amounted to 14.9 g. and showed m.p. 78°, were confirmed to be naphthalene from the melting point and the analytical results of the substance purified by recrystallization from alcohol.

Found: C, 93.62; H, 6.29. Calc. for $C_{10}H_8$: C, 93.75; H, 6.25%.

The liquid portion (7 g.), separated from naphthalene, was supposed to contain some alkyl-naphthalenes, and from it α -methyl-naphthalene⁽⁷⁾ was isolated by recrystallisation from hot alcoholic solution in the form of a yellow crystalline picrate melting at 116-116.5° in a yield of 3.7 g.

Fractions 7 and 8, both being viscous liquids containing some solid substances, were assumed to be mixtures of alkyl-naphthalenes; the isolation of pure substances from the liquids by the formation of picrates was tried but only a red picrate melting at 162-172° was isolated.

Lastly, there was a solid residue which was practically insoluble in alcohol, ether, and benzene, and showed a melting point 242-243° after purified by recrystallization from ether solution. These properties quite agree to those of dianthracene prepared by Graebe and Lieberman, and by

(7) "Beilsteins Handbuch der Organischen Chemie," 4th Ed. Vol. V, p. 567 and Vol. VI, p. 2721, b. p. 242-243°, m.p. 37-38°, picrate m.p. 116-117°.

Ordendorff and Cameron,⁽⁸⁾ from anthracene, and on analysis it gave the following results:

Found: C, 93.85; H, 5.41. Calculated for $(C_{14}H_{10})_2$: C, 94.38; H, 5.61%.

(3) **Quinoline.** When quinoline (50 g.) was heated at 450° for 4 hours with hydrogen of 80 atmospheric pressures, the fall in the pressure was 42.5 atmospheres at 0° and 42.5 g. of a liquid substance besides a gaseous product was obtained. The gas was determined to be of the following composition:

62.4% H_2 , 17.3% CH_4 , 11.5% C_2H_6 , 0.4% C_nH_m . and 8.0% NH_3 .

Through repetition of the same experiments four times, and after removal of lower boiling fractions (below 100°) by distillation, 162.5 g. of the liquid product was obtained. It was then treated with dilute sulphuric acid in order to separate hydrocarbons from bases.

The bases were fractionated into two fractions, and the fraction boiling below 230° was separated by means of meta-phosphoric acid into primary and secondary bases. The yield of each fraction is shown below:

162.5 g.	{	Hydrocarbons	43.0 g.
		Bases {	
	{	below 230° (81.4 g.) {	
		primary	60.5 ,,
		secondary	9.6 ,,
		above 230°	24.6 ,,
		loss	24.8 ,,

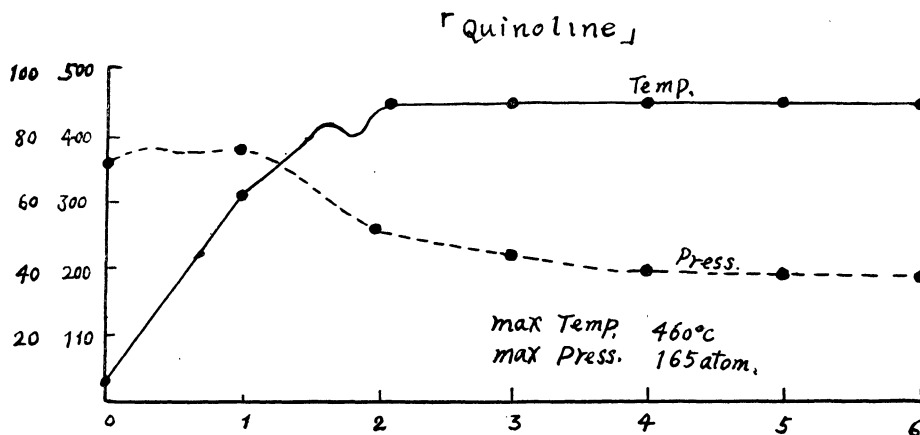


Fig. 4.

(8) *Ann. d. Chem. Spl.*, **7** (1870), 265; *Am. Chem. J.*, **17** (1895), 666.

(a) Primary bases. This fraction (55 g.), set free from the phosphate, was fractionated into 5 fractions with the physical constants given in Table 8.

Table 8.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	180-190	4.8	1.5736	1.0075	Aniline
2	190-200	25.2	1.5731	0.9984	<i>o</i> -Toluidine
3	200-210	9.8	1.5655	0.9842	<i>o</i> -Ethyl-aniline
4	210-220	6.0	1.5612	0.9778	<i>o</i> -Propyl-aniline
5	220-230	3.0	1.5623	0.9860	
Loss		6.2	—	—	

Fractions 1 and 2, as indicated by their physical constants, are assumed to be composed mainly of aniline and of toluidine respectively, and it was confirmed by the melting points of their picrates: 164° and $212-213^\circ$ respectively.

The toluidine showed the physical constants, $d_4^{25} = 0.9950$, and $n_D^{25} = 1.5703$, and gave the following analytical results:

Found: C, 78.37; H, 8.84; N, 12.51. Calc. for C_7H_9N : C, 78.5; H, 8.4; N, 13.1%.

Fractions 3 and 4 were assumed from their physical constants to be composed of ethyl- and propyl-anilines, and it was confirmed by converting them into benzoates melting at $147-148^\circ$ and $117-118^\circ$ respectively. On analysis they gave the following results:

Found: C, 79.49; H, 6.60. Calc. for $C_{16}H_{17}N$: C, 80.00; H, 6.60%.

Found: C, 80.03; H, 6.90. Calc. for $C_{17}H_{19}N$: C, 80.0; H, 7.50%.

(b) Secondary bases. This fraction (9.6 g.) was fractionated as shown in Table 9.

Table 9.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	196-200	1.1	1.5641	0.9792	Methyl- <i>o</i> -toluidine Ethyl- <i>o</i> -toluidine
2	200-210	2.3	1.5601	0.9754	
3	210-220	2.0	1.5520	0.9674	
4	220-230	0.2	1.5538	—	
5	230-240	0.2	—	—	
6	above 240°	3.8	—	—	

Fractions 1, 2, and 3 were assumed from their physical constants to be mixtures of methyl-*o*-toluidine and ethyl-*o*-toluidine, and they gave the following analytical results:

Fraction 2. Found: C, 78.40; H, 9.0. Calc. for $C_8H_{11}N$: C, 79.35; H, 9.09%.

Fraction 3. Found: C, 80.48; H, 8.79. Calc. for $C_9H_{13}N$: C, 80.00; H, 9.63%.

(c) The fraction boiling above 220° was fractionated as shown in Table 10.

Table 10.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	-230	1.2	1.5624	0.9863	Quinoline Methyl-indole
2	230-240	8.7	1.5636	0.9867	
3	240-250	3.0	1.5685	1.0004	
4	250-260	2.3	1.5740	1.0067	
5	260-270	2.0	1.5784	1.0295	
6	above 270°	5.3	—	—	

Fraction 2 was assumed to consist mainly of quinoline from its physical constants, and it was confirmed by transforming it into a picrate of m.p. 203-203.5°, and isolating quinoline (b. p. 207-208°, $n_D = 1.640$, $d_4^{25} = 1.0895$) by the action of alkali on the picrate.

The fraction boiling above 240° gave a sodium salt when heated with metallic sodium or sodium amide. The alcoholic solution of this fraction gave cherry red colour to a pine chip moistened with concentrated hydrochloric acid. These facts indicate that the fraction was a mixture of indole derivatives.

(d) Hydrocarbons. The fraction boiling below 100° was combined with the neutral part of higher boiling points separated from bases, and the whole substance amounted to 43 g. It was fractionated over metallic sodium into 15 fractions as shown in Table 11.

Table 11.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	-70	0.3	—	—	Cyclohexane
2	70-80	1.8	1.4275	0.7655	
3	80-90	1.8	1.4291	0.7666	
4	90-100	0.7	1.4328	0.7780	
5	100-110	1.5	1.4481	0.7935	Methyl-cyclohexane
6	110-120	1.5	1.4662	0.7818	
7	120-130	0.8	1.4661	0.8246	Ethyl-cyclohexane
8	130-140	1.4	1.4080	0.8245	
9	140-150	2.1	1.4730	0.8341	
10	150-160	1.5	1.4733	0.8391	Propyl-cyclohexane
11	160-170	3.0	1.4800	0.8717	
12	170-180	0.8	1.4928	0.8936	
13	180-190	1.6	1.5027	0.9031	
14	190-200	1.0	—	—	
15	Residue	19.4	—	—	

By fractional distillation of fractions 2 and 3, fairly pure cyclohexane (2.1 g., b. p. 80–81°, $n_D^{25} = 1.4281$, $d_4^{25} = 0.7748$) and a mixture of cyclohexane and methyl-cyclopentane were obtained. On analysis the cyclohexane gave the following results :

Found: C, 86.07; H, 13.98. Calc. for C_6H_{12} : C, 85.71; H, 14.29%.

Fractions 4, 5, and 6 were assumed, from their physical constants, to be composed mostly of methyl-cyclohexane with some aromatic hydrocarbons. After washing with concentrated sulphuric acid, redistillation gave a fraction (2.1 g.) with properties (b. p. 102–104°, $n_D^{25} = 1.4358$, $d_4^{25} = 0.7710$) agreeing to methyl-cyclohexane, and on analysis it gave the following result :

Found: C, 85.78; H, 14.10. Calc. for C_7H_{14} : C, 85.71; H, 14.29%.

Fractions 7, 8, and 9 appeared from their physical constants to consist of ethyl-cyclohexane and some aromatic hydrocarbons. After treating them with concentrated sulphuric acid, a fraction (1.2 g., b. p. 132–133°, $n_D^{25} = 1.4479$, $d_4^{25} = 0.7791$) corresponding to ethyl-cyclohexane was isolated.

Found: C, 85.84; H, 13.81. Calc. for C_8H_{16} : C, 85.81; H, 14.29%.

Fractions 10 and 11 were confirmed to be composed mostly of propyl-cyclohexane. By fractional distillation after washing with sulphuric acid, 1.5 g. of the pure substance was obtained. The physical properties and analytical results of the isolated compound were as follows :

B. p. 153–156°; $n_D^{25} = 1.4751$; $d_4^{25} = 0.8347$.

Found: C, 86.00; H, 13.46. Calc. for C_9H_{18} : C, 85.71; H, 14.29%.

Since the residue gave a sodium salt and contained nitrogen, it was assumed to be an indole derivative.

(4) **Isoquinoline.** Isoquinoline (50 g.) was heated at 450° for 4 hours with hydrogen of 80 atmospheric pressures; the fall in the pressure was 33 atmospheres at 0°.

The gas in the autoclave was composed of 59.2 per cent. of H_2 , 15.9 per cent. of CH_4 , 6.9 per cent. of C_2H_6 , 0.5 per cent. of C_nH_m , and 17.1 per cent. of NH_3 . The oily reaction product amounted to 40.4 g. (80.7%).

By repeating similar experiments several times, 282 g. of the liquid reaction product was obtained. It was first separated from the fraction

boiling below 100° , and the higher fraction was then treated with dilute sulphuric acid in order to separate it into basic and neutral substances.

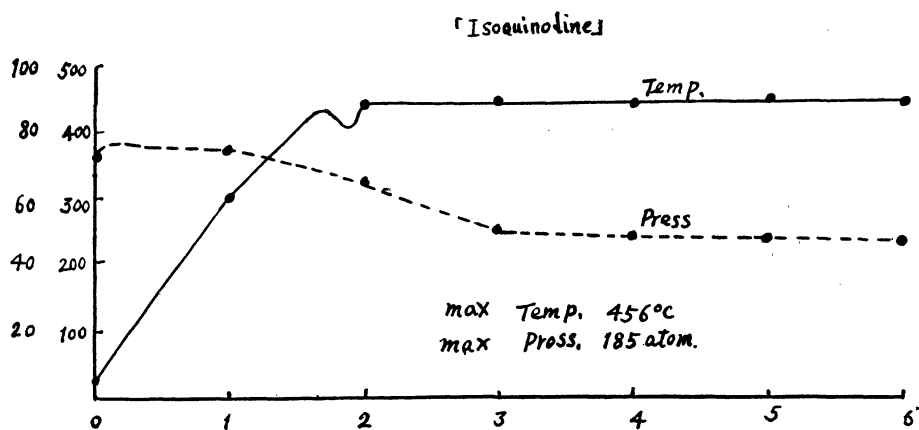


Fig. 5.

(a) Basic substance. The basic substance (65.0 g.) was fractionated into 15 fractions as shown in Table 12.

Table 2.

Fraction	B. p.	Yield (g.)	n_D^{25}	d_4^{25}	Remarks
1	110-120	4.4	1.4928	0.9706	Pyridine
2	120-130	2.2	1.4975	0.9360	Methyl- pyridine
3	130-140	2.0	1.4973	0.8971	
4	140-150	0.9	1.5009	0.8982	
5	150-160	0.6	1.5070	0.9274	Dimethyl- pyridine
6	160-170	—	—	—	
7	170-180	4.2	1.5161	0.9436	
8	180-190	1.6	1.5310	0.9631	} Isoquinoline
9	190-200	1.0	1.5454	0.9821	
10	200-210	—	—	—	
11	210-220	2.5	1.5588	0.9911	
12	220-230	3.0	1.5632	1.0141	
13	230-240	15.1	1.5753	1.0333	
14	240-250	12.1	1.5860	1.0550	
15	250-260	3.4	1.5911	1.0544	

Fraction 1 was composed mostly of pyridine as indicated by its characteristic odour and physical constants. Further it was confirmed by transforming it into a picrate melting at 167° .

Fractions 2, 3, 4, and 5 were composed mostly of methyl-pyridine as seen from physical constants. By deriving a picrate and recrystallizing it from alcohol several times, 0.4 g. of pure methyl-pyridine was obtained. The pure picrate melted at 165° .

Fractions 7, 8, and 9, composed mainly of dimethyl-pyridine, were converted into a picrate to isolate the pure base. The free base (3.4 g.) isolated showed b.p. $176-179^{\circ}$, $n_D^{25} = 1.5161$, and $d_4^{25} = 0.9439$.

Fractions 13 and 14 were composed mostly of isoquinoline as seen from their physical constants. The pure picrate (4.8 g.), isolated from 4.0 g. of these fractions, melted at 223° . The recovered free base (2.7 g.) gave the following analytical results :

Found : C, 83.59; H, 6.18. Calc. for C_9H_7N : C, 83.72; H, 5.42%.

(b) Hydrocarbons. The neutral substance separated from the bases was combined with hydrocarbons boiling below 100° , and the whole amounted to 203 g. It was fractionated by distilling repeatedly over metallic sodium into 10 fractions as shown in Table 13.

Table 13.

Fraction	B. p.	Yield (g.)	d_4^{25}	n_D^{25}	Remarks
1	-100	1.5	—	—	Toluene
2	100-110	1.0	0.7642	1.4308	
3	110-120	10.0	0.8240	1.4771	
4	120-130	2.5	0.8511	1.4941	
5	130-140	2.8	0.8592	1.4960	
6	140-150	26.9	0.8568	1.5000	Xylene
7	150-160	13.8	0.8687	1.5042	
8	160-170	10.8	0.8728	1.5025	Indane
9	170-180	45.9	0.8918	1.5132	
10	180-190	9.3	0.9155	1.5253	

Fractions 3, 6, and 9 were assumed from their physical constants to be composed mostly of toluene, *o*-xylene, and indane respectively.

For the identification of the compounds occurring in these fractions, the substances were oxidized with potassium permanganate, and after purification by distillation they were analyzed with the results given in Table 14.

Table 14.

	Fraction 3	Fraction 6	Fraction 9
B. p.	110-112°	140-145°	172-175°
n_D^{25}	1.4909	1.5009	1.5273
d_4^{25}	0.8539	0.8732	0.9370
Acid obtained by oxidation	Benzoic acid	Phthalic acid	Phthalic acid
Found	C, 91.41; H, 8.92	C, 90.76; H, 9.15	
Calculated	for C_7H_8 C, 91.30; H, 8.70	for C_9H_{10} C, 91.52; H, 8.48	

Lastly, from the final fraction two yellow crystalline substances were obtained, one, amounting to 1.1 g., melted at 202-206°, and the other (2.1 g.) at 239°. The former was confirmed from its analytical results to be α -methyl-anthracene.

Found: C, 93.60; H, 5.89. Calc. for $C_{15}H_{12}$: C, 93.75; H, 6.25%.

In conclusion, the writer wishes to express his sincere thanks to Vice-Admiral Y. Yoshioka, and Rear-Admiral M. Ueda, the former and the present Directors of the Imperial Naval Fuel Depot, and to Rear-Admiral Viscount M. Kawase, and Engineer-Captain R. Kinashi, the former and the present Chiefs of the Scientific Research and Experimental Branch, for their kindness in enabling him to take part in this work, and to Prof. S. Komatsu of the Kyoto Imperial University whose advice and encouragement have been invaluable, and also to Mr. G. Fujii, whose kind assistance enabled him to complete the experiment.

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THE ACTION OF CARBON MONOXIDE ON CHLORO- PLATINIC ACID SOLUTION.

By Isamu SANO.

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The preparation of the colloidal solutions of noble metals such as gold, palladium, and platinum by the action of carbon monoxide on the solutions of their salts was studied by J. Donau.⁽¹⁾ He obtained a red colloidal solution of gold from auric chloride and a black colloidal solution of palladium from palladium chloride. As for the platinum, however, F. C. Phillips⁽²⁾ observed that the blackening of aqueous solutions of platinum chloride by the action of the gas was followed subsequently by slow deposition of metallic platinum.

The present author has obtained red-coloured colloidal solutions of platinum by the action of carbon monoxide on the aqueous solutions of chloroplatinic acid. The present paper describes the experiment on this subject.

Carbon monoxide was prepared by heating the mixture of concentrated sulphuric acid and either formic acid or oxalic acid, the latter being mostly used for the sake of convenience. The gas thus obtained was freed from carbon dioxide by passing through tubes containing caustic alkali. The chloroplatinic acid solution was made by dissolving the acid $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ from Kahlbaum in ordinary distilled water.

On passing carbon monoxide through the aqueous solution of chloroplatinic acid at ordinary temperature for a while, the colour of the solution changes from yellow to red. If a comparatively concentrated solution is used a black solution, instead of red, is obtained. The relation between the concentration of the starting solution and the colour of the resulting solution is shown in Table 1.

It seems, however, that the colour is influenced by the conditions such as temperature, material of the vessel, purity of the gas, etc..

Red solutions thus obtained are always transparent, and have been proved to be colloidal by the Tyndall effect and the experiment of electrophoresis. The particles have the negative charge, and the coagulation values are greatly affected by the valency of the positive ions. Some of the results obtained are tabulated in Table 2.

(1) Donau, *Monatsh.*, **26** (1905), 525; **27** (1906), 59, 71.

(2) Phillips, *Am. Chem. J.*, **16** (1894), 255.

Table 1.

Concentration of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}(\%)$	Colour of resulting solution observed by	
	reflected light	transmitted light
0.2	black	brownish black
0.1	black	brownish black
0.07	black	reddish brown
0.05	black	purplish red
0.04	reddish black	purplish red
0.02	reddish black	purplish red
0.01	reddish black	somewhat light red
0.005	reddish purple	light red

Table 2.

Electrolyte	Coagulation values (milli-mol / litre)	
	Red sol (Author) 0.038 g. Pt per litre	Black sol (Freundlich) 0.14 g. Pt per litre
NaCl	100	2.5
$\frac{1}{2} \text{Na}_2\text{SO}_4$	100	—
$\frac{1}{2} \text{H}_2\text{SO}_4$	—	0.24
BaCl_2	1.5	0.058
MgSO_4	1.5	—
$\text{Al}(\text{NO}_3)_3$	0.02	—
$\frac{1}{2} \text{Al}_2(\text{SO}_4)_3$	0.02	0.013

In order to get the sol free from electrolytes it was dialyzed in distilled water, but the colour always changed to black by this process. The coagulation values were determined in the following manner. Ten cubic centimeters of the aqueous solutions of an electrolyte at various concentrations were mixed, respectively, with 10 c.c. of the sol, and, thus, the minimum amount of that electrolyte sufficient to cause coagulation observable by the naked eye within two hours was decided as the coagulation value of the electrolyte. Table 2 indicates the result with a red sol obtained from a 0.02 per cent. solution of chloroplatinic acid, and accordingly, containing 0.038 gram of platinum in one litre. The third column in the table shows

the result obtained by H. Freundlich⁽³⁾ under nearly the same conditions as the above with a black sol of platinum prepared by Bredig's method. Thus the red sol is more stable than the black one to the action of electrolytes. From Table 2, moreover, it can be seen that the sol is more sensible to the valency of the cation than that of the anion, and, accordingly, the particles in the sol are charged negatively.

In order to get informations of the composition of the colloidal particles in the red sol, the following experiments have been undertaken. The colour of the sol changes from red to black by the following various treatments. (a) On standing the sol in the air, blackening takes place at the surface of the sol and it spreads to the bottom, generally, in less than a few days, producing a black sol of the ordinary appearance. (b) By bubbling oxygen through the sol blackening occurs more rapidly. Hydrogen and nitrogen, however, show no action on the red sol. (c) On the addition of hydrogen peroxide the sol immediately undergoes the same colour change as the above, bubbles being evolved actively. (d) If the sol is kept in an large evacuated vessel the colour change from red to black is slow, taking a period of several days; and on taking it out subsequently to the outer atmosphere, it turns black in a short time. (e) If the sol is kept in a sealed test tube the red colour is stable during a considerable period. Some of the samples have been kept unchanged for the period of nine months already.

From these experiments it was ascertained that the colour of the sol is affected by the oxidizing action of oxygen. The blackening of the red sol might probably occur as a result of the disappearance of carbon monoxide in the sol due to the action of oxygen. This can be confirmed by the following observations. (f) If heated on a water bath, the red sol, turning brown at moderate temperature, becomes black at about 95°C., slight bubble-formation being sometimes observed. (g) On mixing alcohols or acetone with the red sol, bubbles are produced immediately, and then the colour changes to black within a few hours or so. Carbon monoxide, thus, seems to be one of the essential components of the red sol.

Some considerations of the structure of these colloidal particles have been made as follows. Since carbon monoxide is an essential component of the sol, an intuitive model representing the structure of the colloidal particles in the sol may be such as shown by Fig. 1a. According to this model, particles are constructed with a great number of platinum atoms surrounded by platinum carbonyl molecules $\text{Pt}(\text{CO})_n$. According to the

(3) Freundlich *Z. physik. Chem.*, **44** (1903), 152.

studies of Schützenberger and others,⁽⁴⁾ there exists such a compound as $\text{Pt}(\text{CO})\text{Cl}_2$, which is so unstable in dilute aqueous solution that it decomposes immediately into platinum, carbon dioxide, and hydrochloric acid, but is considerably stable in concentrated hydrochloric acid as it forms a compound such as $[\text{Pt}(\text{CO})\text{Cl}_3]\text{H}$. Therefore, another structure expressed by Fig. 1 b might be expected in the presence of concentrated hydrochloric acid. According to this model, a group of platinum atoms forms the centre

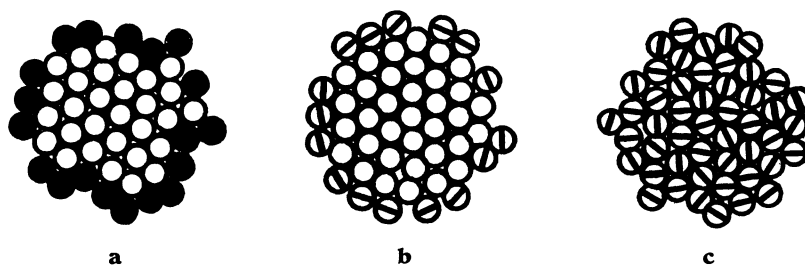


Fig. 1.

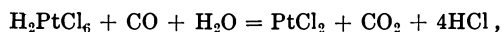
of a particle and is surrounded by $[\text{Pt}(\text{CO})\text{Cl}_3]$ -ions. Since chloroplatinic acid solutions used were always dilute throughout the experiment, such a complex compound as described above must have been unable to exist as a stable one, and the decomposition of it must have been inevitable. Moreover, if the red sol were given by the particles of this structure, the red sol must have been obtained with a concentrated chloroplatinic acid solution which might afford concentrated hydrochloric acid. The experimental results are contrary to this supposition as can be seen from Table 1.

Now the following experiments have been undertaken. On the addition of a small quantity of very dilute bromine water to the red sol, it became at once discoloured to be faintly yellow. The solution thus obtained never displays the Tyndall effect even immediately after mixing. But, if a suitable amount of bromine water is added, the solution proves to show the Tyndall effect distinctly after heated for a while or left over night at room temperature. Again, if an excess of bromine water is added the Tyndall effect is never observed. These phenomena may be accounted for in the following manner by assuming that the particles in the red sol are of the structure represented by Fig. 1 c.

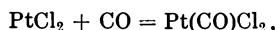
(4) Schützenberger, *Ann. chim. phys.*, [4], **21** (1870), 350; *J. prak. Chem.*, [2], **4** (1871), 159. Pullinger, *Ber.*, **24** (1891), 2291; *J. Chem. Soc.*, **59** (1891), 598. Mylius and Foerster, *Ber.*, **24** (1891), 2424.

Some experimental facts have been reported to indicate the formation of platinum carbonyl such as $\text{Pt}(\text{CO})_n$, though this compound has not yet been isolated.⁽⁵⁾ From the general properties of the metal carbonyls, the compound may be sparingly soluble or insoluble in water and decomposed by the aqueous solution of halogens. The insolubleness in dispersing medium is, of course, the essential condition of colloid formation.

Thus, the following reactions may be considered as showing the mechanisms of the formation of colloidal particles of the sol. Platinous chloride may be formed by the reaction,



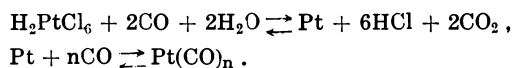
and, subsequently, platinum carbonyl chloride may be formed by the reaction,



which is immediately decomposed by water, depositing platinum of molecular dimension. This may combine, as soon as it is formed, with carbon monoxide existing excessively around it to produce platinum carbonyl $\text{Pt}(\text{CO})_n$. The carbonyl molecules thus formed have a strong tendency to condense themselves for colloid formation, and produce the red sol. Hence, the following equilibria may be established in the solution.



Fig. 2.



The following observations support the above assumptions. The electrical conductivities of chloroplatinic acid solutions were measured at 25°C. by means of a Wheatstone bridge with simultaneous recording of time. The carbon monoxide gas was passed through the solution with constant velocity. The reaction vessel was used, at the same time, as the conductivity cell as shown in Fig. 2. The capacity of the vessel was about 30 c.c. The blank platinum electrodes were used. Some of the results obtained are given in Table 3 and Fig. 3. The concentration of the chloroplatinic acid solution was 0.02 per cent. and the rate of passage of the carbon monoxide gas was 3.0–3.5 litres per hour.

(5) Mond, Langer, and Quincke, *Chem. News*, **62** (1890), 97.
Harbeck and Lunge, *Z. anorg. Chem.*, **16** (1897), 50.

Table 3.

Time (min.)	Specific conductivity (mho.)	Colour of solution
0	367.8×10^{-6}	faintly yellow
30	376.6	—
60	403.2	—
90	454.2	slightly dark
99	906.2	dark red
102	941.6	red
120	993.0	—
150	998.7	—
270	1012.0	—
The gas bubbling was discontinued, and the sol was left in the air.		
48 hrs.	1012.1×10^{-6}	upper part black, lower part red
72 hrs.	1011.4	black uniformly

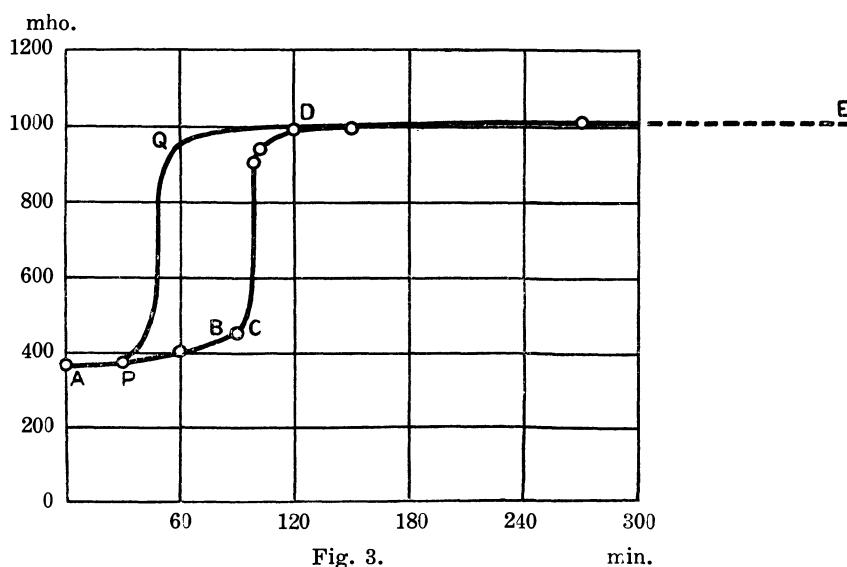


Fig. 3.

min.

The solution is of yellow tint at the period of AB in Fig. 3. At point B it begins to become somewhat dark, at C it becomes red suddenly, and then at D the sol takes the deepest colour. If the bubbling of carbon monoxide

is discontinued at point D, and the red sol obtained is exposed to the air for a few days, it turns black at its upper layer, though it shows the same electrical conductivities as before. This is represented by point E in Fig. 3. If the rate of passage of the gas is changed, another curve as shown by APQDE is obtained.

Moreover, the following facts were observed. If bubbling of carbon monoxide is interrupted at point B, the solution of a black tint thus obtained does not or hardly show the Tyndall effect then and there. But in a few minutes it turns orange and at the same time proves to display the Tyndall effect distinctly. The more distinct the Tyndall effect becomes, the deeper the colour turns. At last a solution of brown colour is obtained. This brown solution cannot be turned to red by the passage of carbon monoxide. The brown solution is considered to be a mixed sol of platinum and its carbonyl.

It will be seen from the above observation that if bubbling of carbon monoxide is once interrupted, it fails to obtain a red solution. This may be explained as follows: It is not possible for platinum molecules to form carbonyl owing to the strong tendency of the formation of platinum colloid, if the amount of carbon monoxide is not sufficient to produce the carbonyl. Thus it may be concluded that most of the particles in the red sol have the structure represented by Fig. 1 c.

Summary.

(1) By passing carbon monoxide gas through the dilute aqueous solution of chloroplatinic acid, a red-coloured colloidal solution was obtained.

(2) The red sol was more stable than the ordinary black platinum sol against electrolytes.

(3) The red sol changed to the black one evolving some gas bubbles by the action of air, oxygen, hydrogen peroxide, alcohols, and acetone, or by the process of evacuation or heating.

(4) The action of bromine water on the red sol is described.

(5) The change of the electrical conductivity was measured in the process of formation of the red sol.

(6) The structure of the colloidal particles of the red sol is discussed. They consist, probably, of groups of platinum carbonyl molecules.

The author wishes to express his cordial thanks to Professor J. Same-shima, under whose kind guidance this work has been carried out.

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STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES. PART III. RAMAN EFFECT OF α -MONO-DERIVATIVES OF FURAN.

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Introduction.

As to the Raman effect of hetero-cyclic compounds with five-membered rings, comparatively few papers have been published. Thiophene and pyrrole have been recently studied by S. Venkateswaran,⁽¹⁾ pyrrole and its derivatives by G. B. Bonino,⁽²⁾ and some oxydiazole derivatives by M. Milone.⁽³⁾ The present authors have investigated the Raman effect of furan derivatives in order to find the characteristic Raman lines associated with the furan ring, to find the influences exerted by the groups attached to it, and to confirm the molecular constitution of the furan ring. Ten α -mono-derivatives of furan, viz., α -methyl-furan, α -furfuryl alcohol, α -furfuryl acetate, α -furfural, α -furoyl chloride, methyl α -furoate, ethyl α -furoate, α -furfuracrylic acid, ethyl α -furfuracrylate, and tetrahydro- α -furfuryl alcohol, were examined and the results are reported in the present paper. Furfural has been re-examined to compare the results with the data obtained by K.W.F. Kohlrausch and his co-workers⁽⁴⁾ and other authors.⁽⁵⁾

Experimental.

A spectrograph with three prisms, constructed in our laboratory, was used in the present experiments. The dispersion obtained was 10 Å. per mm. at 4000 Å. and 20 Å. per mm. at 5000 Å., and the experiments were carried out over the range between these extremities. Most of the materials used have been synthesized in our laboratory.

(1) S. Venkateswaren, *Indian J. Phys.*, **5** (1930), 145; **7** (1933), 585.

(2) G. B. Bonino, R. Manzoni-Ansidei, and P. Pratesi, *Z. physik. Chem.*, (B), **22** (1933), 21-44.

(3) M. Milone, *Gazz. chim. ital.*, **63** (1933), 334; **63** (1933), 456.

(4) K.W.F. Kohlrausch, A. Pongratz, and R. Seka, *Ber.*, (B) **66** (1933), 11.

(5) S.S. Lu, *ibid.*; *Sc. Rep. Nat. Tsing Hua Univ.*, **1** (1931), 25; George Glockler and B. Wiener, *J. Chem. Phys.*, **2** (1934), 47.

α -Methyl-furan⁽⁶⁾ (b. p. 64°C.) was prepared by Wolff-Kischner's method, that is, by dropping a small piece of potassium hydroxide into a mixture of furfural, hydrazine hydrate, and methyl alcohol, under sufficient cooling (-30°C.). The substance obtained was washed with a saturated aqueous solution of calcium chloride, dehydrated over calcium chloride, and then redistilled over metallic sodium under the normal pressure.

α -Furfuryl acetate⁽⁷⁾ (b.p. 65°/5 mm.) was prepared from α -furfuryl alcohol and acetic anhydride in the presence of fused sodium acetate.

α -Furoyl chloride (b.p. 78°/30 mm.) was made by warming α -furoic acid with thionyl chloride.

Methyl α -furoate (b.p. 57°/5 mm.) and ethyl α -furoate (m.p. 34°, b.p. 78°/8 mm.) were made from α -furoyl chloride with absolute methyl and ethyl alcohols respectively, in the presence of pyridine.

A benzene solution of ethyl α -furoate ($1/10$ mol) was used for the experiment, as the substance is solid at ordinary temperature.

α -Furfuracrylic acid⁽⁸⁾ (m.p. 141°C.) was synthesized from furfural, acetic anhydride, and fused sodium acetate (Perkin's method). The recrystallized substance was dissolved in alcohol ($1/15$ mol) and used for the experiment of Raman spectra.

Ethyl α -furfuracrylate (b.p. 100°/5 mm.) was prepared by warming a mixture of the silver salt of α -furfuracrylic acid and methyl iodide.

Commercial pure α -furfuryl alcohol and tetrahydro- α -furfuryl alcohol made by Takeda, and furfural made by Merck, were used. All the liquid substances were purified by repeated vacuum distillation after washing and dehydrating.

The results are shown in the accompanying tables I—X and graphically in Fig. 1. In Table A, indices to tables and plates, the numbers of the Raman lines, and the conditions under which the spectra were taken are given for each substance.

About 10 c.c. of each substance was used. In the case of tetrahydro- α -furfuryl alcohol, the observation of the Raman lines was difficult, for most of the lines were so diffuse and broad that an accurate measurement was impossible. During the exposure under the mercury light for two or three hours, α -furfuryl alcohol, furfural, α -furoyl chloride, α -furfuracrylic acid, and its ethyl ester were coloured in faint yellow or brown, so that a redistilled, fresh substance was necessary to continue the exposure for a sufficient time. Even so, most of the lines in the range shorter than 4358

(6) Tadeus Reichstein, *Helvetica Chim. Acta*, **13** (1930), 345; Wolff-Kischner, *Ann.*, **394** (1912), 86.

(7) L. von Wiessel and B. Tollens, *Ann.*, **272** (1893), 303.

(8) Adolf Baeyer, *Ber.*, **10** (1877), 357.

Å. could not be well observed on account of the colouration. By using a saturated solution of sodium nitrite as a filter the back ground of the plates was removed.

The results on furfural obtained by W.K.F. Kohlrausch,⁽⁹⁾ S.S. Lu,⁽¹⁰⁾ and G. Glockler and B. Wiener⁽¹¹⁾ are compared with ours in Table B.

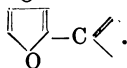
Discussion of the Results.

The Raman lines corresponding to the frequencies of $\Delta\nu$, 888, 925, 1020, 1081, 1153, 1232, 1390, 3122, and 3153 cm^{-1} , appear intense in all the α -derivatives of furan, which may be considered as the characteristic lines of these substances. The weak Raman lines in the region between $\Delta\nu$, 625 and 650 cm^{-1} , and the intense lines of $\Delta\nu$, 888, 1088, and 1390 cm^{-1} , were observed also in thiophene, and pyrrole and its derivatives, though they were not observed in such good constancy as in the case of α -derivatives of furan.

The lines in the region between $\Delta\nu$, 1460 and 1605 cm^{-1} , seem to be note-worthy in the case of furan derivatives as well as pyrrole derivatives. In α -methyl-furan, α -furfuryl alcohol, and α -furfuryl acetate, two intense lines of $\Delta\nu$, 1507 and 1605 cm^{-1} , are observed, while in methyl α -furoate, ethyl α -furoate, ethyl α -furfuracrylate, and α -furfuracrylic acid, two lines of $\Delta\nu$, 1477 and 1572 cm^{-1} , are observed. From these facts, it is considered that the frequencies of 1507 and 1605 cm^{-1} can be attributed to the type of



while the frequencies of 1477 and 1572 cm^{-1} , to the type of



The high frequency of 1641 cm^{-1} in furfuracrylic acid and its ethyl ester seems to be attributable to the $-\text{CH}:\text{CH}-$ linkage in the side chain. In the study of pyrrole and its derivatives, G.B. Bonino and his co-worker⁽¹²⁾ have reported that the frequencies of $\Delta\nu$, 1136 and 1466 cm^{-1} , are attributed to the vibration between the two carbon-atoms in β - and β' -positions and CH-groups in α - and α' -positions of the pyrrole ring, respectively. And they have considered that the frequency of 1550 cm^{-1} is associated with the central vibration, giving a formula of pyrrole like the following :

(9) Cf. (4).

(10) S. S. Lu, *Sc. Rep. Nat. Tsing Hua Univ.*, **1**, (1931), 25.

(11) G. Glockler and B. Wiener, *J. Chem. Phys.*, **2** (1934), 47.

(12) G. B. Bonino and his co-worker, *Z. physik. Chem.*, (B) **22** (1933), 42.

Table A.

Substance	No. of Table	No. of Raman lines	No. of Plate	Width of slit (10 ⁻² mm.)	Electric current (amp.)	Temperature (C.)	Time of exposure (hours)
α -Methyl-furan	I	53	148	80	4.0	20	5
			149	72	4.2	20	12
			171	70	4.0	15	8
			186	64	4.2	19	15
α -Furfuryl alcohol	II	39	128	90	3.5	24	7
			168	64	4.0	15	10
			206	70	3.8	22	16
α -Furfuryl acetate	III	40	179	70	4.0	19	7
			182	64	4.0	19	5
			193	70	4.0	19	10
			194	80	4.0	19	8
α -Furfural	IV	54	195	76	4.2	20	6
			198	64	4.2	20	8
			202	64	4.0	21	10
α -Furoyl chloride	V	29	178	70	4.0	19	5
Methyl α -furoate	VI	55	146	90	3.8	21	6
			199	70	4.2	20	10
			209	64	3.8	22	15
Ethyl α -furoate (in benzene)	VII	59	207	70	3.8	22	10
			208	64	3.8	22	16
α -Furfuracrylic acid (in alcohol)	VIII		139	80	4.0	25	14
			200	76	4.2	21	12
			201	70	4.0	21	16
Ethyl α -furfuracrylate	IX	36	184	70	4.0	20	6
			197	70	4.0	20	7
			212	64	4.0	23	12
			213	76	4.0	23	16
Tetrahydro- α -furfuryl alcohol	X		169	64	4.0	15	8
			170	70	4.0	15	7
			190	76	4.0	20	12

Table B. Comparison of the results on furfural.

Lu	Kohlrausch	Glockler	Matsuno and Han
—	—	172	162 (4, <i>b</i> , <i>d</i>)
282 (1)	—	—	213 (3)
493 (1)	501 (3)	497	503 (7)
—	—	581	598 (2)
—	—	624	630 (2)
—	—	758	749 (3 <i>d</i>) 775 (1 <i>d</i>)
—	881 (3)	878	882 (7 <i>s</i>)
—	928 (3)	929	928 (8 <i>s</i>)
—	—	—	946 (4)
—	1018 (5)	1021	1019 (8)
—	1076 (3)	1078	1080 (7)
—	1147 (5)	1156	1151 (6) 1159 (7)
—	1212 (2)	—	—
—	—	1221	1207 (1) 1223 (4 <i>d</i>)
—	—	—	(1275) (2)
1369 (7)	1359 (10)	1378	1368 (10)
—	1384 (8)	—	1393 (10)
—	—	—	1441 (2)
1461 (7)	1461 (15)	1467	1463 (10) 1475 (10)
—	—	—	1484 (1)
1500 (2)	1561 (4)	1567	1568 (8)
1662 (3)	1665 (15) 1683 (10)	1677	1668 (10 <i>b</i>) 1688 (8, <i>b</i> , <i>d</i>)
—	—	2881	(3123) (4)
2998 (3)	—	3129	(3151) (2)

Table I.
 α -Methyl-furan, $C_4H_5O \cdot CH_3$.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	24463	4 (<i>d</i>)	<i>q</i> -2925 (<i>k</i> -242)	28	22049	3	<i>e</i> -889
2	24426	2 (<i>d</i>)	<i>q</i> -2962 (<i>p</i> -2927)	29	22021	4	<i>e</i> -917
3	24365	1 (<i>d</i>)	<i>k</i> -340	30	21962	2	<i>k</i> -2743 (<i>e</i> -976) ?
4	24270	1 (<i>d</i>)	<i>q</i> -3118	31	21920	3	<i>e</i> -1018
5	24235	1 (<i>d</i>)	<i>q</i> -3153 (<i>p</i> -3118)	32	21854	8 (<i>s</i>)	<i>e</i> -1084
6	24078	1	<i>k</i> -627	33	21816	3	<i>k</i> -2889
7	24052	2	<i>k</i> -653	34	21791	3	<i>e</i> -1147
8	23818	1/2	<i>k</i> -887	35	21776	7	<i>k</i> -2929
9	23787	1	<i>k</i> -918	36	21751	2 (<i>d</i>)	<i>k</i> -2954
10	23687	1/2 (<i>d</i>)	<i>k</i> -1018	37	21723	4	<i>e</i> -1215
11	23621	6 (<i>s</i>)	<i>k</i> -1084	38	21705	3	<i>e</i> -1233 (<i>k</i> -3000)?
12	23558	2 (<i>d</i>)	<i>k</i> -1147	39	21586	6 (<i>d</i>)	<i>k</i> -3119
13	23490	2	<i>k</i> -1215	40	21562	3 (<i>d</i>)	<i>e</i> -1376
14	23471	1	<i>k</i> -1234	41	21549	6 (<i>d</i>)	<i>e</i> -1389 (<i>k</i> -3156)
15	23436?	1/2	<i>i</i> -1080	42	21486	4 (<i>d</i>)	<i>e</i> -1452 (<i>f</i> -1509)
16	23329	3	<i>k</i> -1376	43	21428	10	<i>e</i> -1510
17	23316	3	<i>k</i> -1389	44	21394	1	<i>i</i> -3122 (<i>f</i> -1601)
18	23251	4	<i>k</i> -1454	45	21363	1	<i>i</i> -3153
19	23194	8	<i>k</i> -1511	46	21334	6	<i>e</i> -1604
20	23100	5	<i>k</i> -1605	47	20191	1	<i>e</i> -2747
21	22685	5 (<i>d</i>)	<i>e</i> -253	48	20051	1	<i>e</i> -2887
22	22595	3 (<i>d</i>)	<i>e</i> -343	49	20010	5	<i>e</i> -2928
23	22312	3	<i>e</i> -626	50	19982	1	<i>e</i> -2956
24	22284	6	<i>e</i> -654	51	19937?	1/2	<i>e</i> -3001
25	22220	1 (<i>b, d</i>)	<i>e</i> -718	52	19815	3	<i>e</i> -3123
26	22142	1 (<i>d</i>)	<i>e</i> -796	53	19785	2	<i>e</i> -3153
27	22083	1 (<i>d</i>)	<i>e</i> -855 (<i>f</i> -912)				

$\Delta\nu$: 253 (5*d*); 343 (3*d*); 626 (3); 654 (6); 718 (1*b, d*); 796 (1*d*); (855) (1*d*); 888 (3); 917 (4); (976) (2)?; 1018 (3); 1084 (8*s*); 1147 (3); 1215 (4); 1233 (3); 1376 (3); 1389 (6*d*); 1453 (4*d*); 1510 (10); 1605 (6); 2745 (2); 2888 (3); 2928 (7); 2955 (2*d*); 3000 (1)?; 3119 (6*d*); 3153 (4*d*).

Table II.

 α -Furfuryl alcohol, $C_4H_3O \cdot CH_2OH$.

No.	ν (cm. ⁻¹)	I	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	I	$\nu_0 - \Delta\nu$
1	23816	$1/2$	k -889	21	21979	$1/2$	e -959
2	23783	0	k -922	22	21920	2 (b, d)	e -1018
3	23687	$1/2$ (d)	k -1018	23	21855	6	e -1083
4	23623	2	k -1082	24	21825	1 (d)	k -2880
5	23552	1 (d)	k -1153	25	21784	3 (d)	e -1154
6	23478	2	k -1227	26	21710	4	e -1228
7	23440	$1/2$ (d)	k -1265	27	21669	1 (d)	e -1269
8	23328	1 (d)	k -1377	28	21587	4 (d)	k -3118
9	23312	2 (d)	k -1393	29	21567	1	e -1371
10	23225	1 (bb)	k -1480	30	21548	4 (d)	e -1390 (k -3157)
11	23198	6	k -1507	31	21463	2 (b, d)	e -1475
12	23104	4	k -1601	32	21431	8	e -1507
13	22761	4 (d)	e -177	33	21396	1	i -3120
14	22517	1 (b, d)	e -421	34	21363	1 (d)	i -3153
15	22335	$1/2$ (d)	e -603	35	21336	4 (d)	e -1602
16	22312	2 (d)	e -626	36	21066	1 (d)	e -2872
17	22197 ?	0 (d)	e -741	37	19998	2 (b, d)	e -2940
18	22122 ?	0 (d)	e -816	38	19821	4	e -3117
19	22051	3	e -887	39	19787	3	e -3151
20	22016	2	e -922				

$\Delta\nu$: 177 (4d); 421 (1b, d); 603 ($1/2$); 626 (2d); 741 (0d)?; 816 ($1/2$ d); 888 (3); 922 (2); 959 ($1/2$); 1018 (2b, d); 1083 (6); 1154 (3d); 1228 (4); 1267 (1d) 1374 (1); 1391 (4d); 1477 (2b, d); 1507 (8); 1602 (4d), 2876 (1d); 2940 (2b, d)?; 3117 (4); 3154 (3).

Table III.

 α -Furfuryl acetate, $C_4H_3O \cdot CH_2O \cdot OC \cdot CH_3$.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
	24046	$1/2$ (<i>d</i>)	<i>k</i> -659	22	22103	1(<i>b</i> , <i>d</i>)	<i>e</i> -835 (<i>f</i> -892)
2	23821	1	<i>k</i> -884	23	22052	5	<i>e</i> -886
3	23782	2 (<i>d</i>)	<i>k</i> -923	24	22013	4	<i>e</i> -925
4	23738	0 (<i>d</i>)	<i>k</i> -967	25	21974	1	<i>e</i> -964
5	23683	2 (<i>d</i>)	<i>k</i> -1022	26	21916	4	<i>e</i> -1022
6	23623	3	<i>k</i> -1082	27	21855	6	<i>e</i> -1083
7	23581	1(<i>b</i> , <i>d</i>)	<i>k</i> -1124 (<i>i</i> -935)	28	21784	1	<i>e</i> -1154
8	23553	3 (<i>d</i>)	<i>k</i> -1152	29	21759	4	<i>k</i> -2946
9	23473	2 (<i>d</i>)	<i>k</i> -1232	30	21708	3	<i>e</i> -1230
10	23439	$1/2$ (<i>d</i>)	<i>i</i> -1077	31	21577	6 (<i>d</i>)	<i>k</i> -3128
11	23320	3	<i>k</i> -1385	32	21545	6 (<i>d</i>)	<i>e</i> -1393 (<i>k</i> -3160)
12	23199	6	<i>k</i> -1506	33	21488	2 (<i>d</i>)	<i>e</i> -1450 (<i>f</i> -1507)
13	23129	1 (<i>d</i>)	<i>i</i> -1387	34	21434	8	<i>e</i> -1504
14	23102	4	<i>k</i> -1603	35	21393	$1/2$	<i>i</i> -3123 (<i>f</i> -1602)
15	22766 ?	$1/2$ (<i>d</i>)	<i>e</i> -172	36	21333	6	<i>e</i> -1605
16	22745 ?	1 (<i>d</i>)	<i>e</i> -193	37	21193	2 (<i>d</i>)	<i>e</i> -1745
17	22623 ?	$1/2$ (<i>d</i>)	<i>e</i> -315	38	19993	4	<i>e</i> -2945
18	22606	$1/2$ (<i>d</i>)	<i>e</i> -332	39	19809	4	<i>e</i> -3131
19	22317	3 (<i>d</i>)	<i>e</i> -621	40	19782	2 (<i>d</i>)	<i>e</i> -3156
20	22279	4	<i>e</i> -659				
21	22193	1 (<i>d</i>)	<i>e</i> 745				

$\Delta\nu$: 172 ($1/2d$)?; 193 ($1/2d$)?; 315 ($1/2d$)?; 332 ($1/2$); 621 (3*d*); 659; 659 (4); 745 (1*d*)?; 835 (1*b*, *d*)?; 886 (5); 924 (4); 964 (1); 1022 (4); 1083 (6); 1153 (1); 1231 (3); 1389 (6*d*); 1450 (2*d*); 1505 (8); 1604 (6); 1745 (3*d*); 2946 (4); 3130 (6*d*); 3156 (3).

Table IV.
 α -Furfural, $C_4H_3O \cdot CO \cdot H$.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	24203	2	<i>k</i> -502	28	22189	3 (<i>d</i>)	<i>e</i> -749
2	23822	2	<i>k</i> -883	29	22163	1 (<i>d</i>)	<i>e</i> -775
3	23774	3	<i>k</i> -931	30	22056	7 (<i>s</i>)	<i>e</i> -882
4	23760	1	<i>k</i> -945	31	22012	8 (<i>s</i>)	<i>e</i> -926
5	23687	4	<i>k</i> -1018	32	21992	4	<i>e</i> -946
6	23625	2 (<i>d</i>)	<i>k</i> -1080	33	21918	8	<i>e</i> -1020
7	23550	3 (<i>d</i>)	<i>k</i> -1155	34	21858	7	<i>e</i> -1080
8	23500	1/2	<i>k</i> -1205	35	21787	6	<i>e</i> -1151
9	23443 ?	0	<i>i</i> -1073	36	21779	7	<i>e</i> -1159
10	23357	0	<i>i</i> -1159	37	21729	0	<i>e</i> -1209
11	23338	7	<i>k</i> -1367	38	21715	4 (<i>d</i>)	<i>e</i> -1223
12	23312	7	<i>k</i> -1393	39	21663	2	<i>e</i> -1275
13	23262	1/2	<i>k</i> -1443	40	21625	2	<i>f</i> -1370
14	23241	8	<i>k</i> -1464	41	21601	3	<i>f</i> -1394
15	23229	8	<i>k</i> -1476	42	21570	10	<i>e</i> -1368
16	23220	1	<i>k</i> -1485	43	21545	10	<i>e</i> -1393
17	23149	2	<i>i</i> -1367	44	21498	2	<i>e</i> -1440
18	23136	4	<i>k</i> -1569	45	21476	10	<i>e</i> -1462
19	23122	2	<i>i</i> -1394	46	21465	10	<i>e</i> -1473
20	23054	1	<i>i</i> -1462	47	21456	1	<i>e</i> -1482
21	22832	3 (<i>b, d</i>)	<i>f</i> -163	48	21371	8	<i>e</i> -1567
22	22776	4 (<i>b, d</i>)	<i>e</i> -162	49	21323	2	<i>f</i> -1672
23	22725	3	<i>e</i> -213	50	21297	2	<i>f</i> -1698
24	22636	1/2	<i>e</i> -302	51	21270	10 (<i>b</i>)	<i>e</i> -1668
25	22435	7	<i>e</i> -503	52	21250	8 (<i>b, d</i>)	<i>e</i> -1688
26	22340	2	<i>e</i> -598	53	19815	4	<i>e</i> -1523
27	22308	2	<i>e</i> -630	54	19787	2	<i>e</i> -3151

$\Delta\nu$; 162 (4, *b, d*); 213 (3); 302 (1/2); 503 (7); 598 (2); 630 (2); 749 (3*d*); 775 (1*d*); 882 (7*s*); 928 (8*s*); 946 (4). 1019 (8); 1080 (7); 1151 (6); 1159 (7); 1207 (1); 1223 (4*d*); (1275) (2); 1368 (10); 1393 (10); 1441 (2); 1463 (10); 1475 (10); 1483 (1); 1568 (8); 1668 (10*b*); 1688 (8, *b, d*); (3123) (4); (3151) (2).

Table V. Furoyl chloride, $C_4H_3O \cdot CO \cdot Cl$.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	23682	$\frac{1}{2}$	<i>k</i> -1023	16	22051	4	<i>e</i> -887
2	23626	$\frac{1}{2}$	<i>k</i> -1079	17	21988	4	<i>e</i> -950
3	23541	2	<i>k</i> -1164	18	21910	5 (<i>d</i>)	<i>e</i> -1028
4	23490	0 (<i>d</i>)	<i>i</i> -1026	19	21854	5	<i>e</i> -1084
5	23318	5	<i>k</i> -1387	20	21775	5 (<i>d</i>)	<i>e</i> -1163
6	23245	8 (<i>b, d</i>)	<i>k</i> -1460	21	21706	3	<i>e</i> -1232
7	23146	2 (<i>s</i>)	<i>k</i> -1559	22	21684 ?	$\frac{1}{2}$	<i>e</i> -1254
8	23127	2 (<i>d</i>)	<i>i</i> -1389	23	21576	1 (<i>b, d</i>)	<i>k</i> -3129
9	23053	2	<i>i</i> -1463	24	21549	8 (<i>d</i>)	<i>e</i> -1389 (<i>k</i> -3156)
10	22747	4 (<i>b, d</i>)	<i>e</i> -191 (<i>i</i> -1769)	25	21479	10 (<i>d</i>)	<i>e</i> -1459
11	22602	3	<i>e</i> -336	26	21377	4	<i>e</i> -1561
12	22511	4	<i>e</i> -427	27	21194	8 (<i>b, d</i>)	<i>e</i> -1744
13	22386	6	<i>e</i> -552	28	21161	4 (<i>b, d</i>)	<i>e</i> -1777 ?
14	22153 ?	1 (<i>b, d</i>)	<i>e</i> -780	29	19810	$\frac{1}{2}$ (<i>d</i>)	<i>e</i> -3128
15	22114	2 (<i>b, d</i>)	<i>e</i> -824				

$\Delta\nu$: 191 (4*b, d*); 336 (3); 427 (4); 552 (6); 785 (1*b, d*)?; 824 (2*b, d*)? 887 (4); 950 (4); 1025 (5*d*); 1084 (5); 1163 (5*d*); 1232 (3); 1254 ($\frac{1}{2}$)?; 1388 (8*d*); 1460 (10*d*); 1560 (4); 174 (8*b, d*); 1777 (4*b, d*); 3129 (1*b, d*),

Table VI. Methyl α -furoate, $C_4H_3O \cdot CO \cdot O \cdot CH_3$.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	24468	1	<i>k</i> -237	13	23782	4	<i>k</i> -923
2	24426	2	<i>q</i> -2962	14	23687	4 (<i>d</i>)	<i>k</i> -1018
3	24372	$\frac{1}{2}$ (<i>b</i>)	<i>k</i> -331	15	28624	4	<i>k</i> -1081 (<i>i</i> -892)
4	24312	2 (<i>d</i>)	<i>k</i> -393	16	23582	4 (<i>d</i>)	<i>k</i> -1123
5	24259	$\frac{1}{2}$ (<i>d</i>)	<i>q</i> -3129	17	23532	4 (<i>b, d</i>)	<i>k</i> -1173
6	24227	$\frac{1}{2}$ (<i>b, d</i>)	<i>q</i> -3161 (<i>p</i> -3126)	18	23502	1 (<i>b, d</i>)	<i>i</i> -1014
7	24092	0	<i>k</i> -613	19	23465	3	<i>k</i> -1240
8	24080	0	<i>k</i> -625	20	23443	1 (<i>d</i>)	<i>i</i> -1073
9	23932	$\frac{1}{2}$	<i>k</i> -773	21	23396	2 (<i>d</i>)	<i>k</i> -1309 (<i>i</i> -1126)
10	23906	3	<i>k</i> -799	22	23314	6 (<i>b</i>)	<i>k</i> -1391
11	23816	3	<i>k</i> -889	23	23227	8 (<i>b</i>)	<i>k</i> -1478
12	23793	3	<i>k</i> -912				

Table VI.—(Concluded)

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
24	23131	4	<i>k</i> -1574 (<i>i</i> -1385)	41	21817	5 (<i>b, d</i>)	<i>e</i> -1121
25	23120	5	<i>k</i> -1585	42	21767	4 (<i>b, d</i>)	<i>e</i> -1171
26	22792	2(<i>b, dd</i>)	<i>i</i> -1724	43	21747	5 (<i>b, d</i>)	<i>k</i> -2958
27	22763	2 (<i>dd</i>)	<i>e</i> -170 (<i>f</i> -227)	44	21705	5	<i>e</i> -1233
28	22705	5 (<i>b, d</i>)	<i>e</i> -233	45	21632	4	<i>e</i> -1306
29	22599	1/2	<i>e</i> -339	46	21582	4	<i>k</i> -3123
30	22540	4	<i>e</i> -398	47	21548	8 (<i>b</i>)	<i>e</i> -1390 (<i>k</i> -3157)
31	22445	3	<i>e</i> -493	48	21460	10 (<i>bb</i>)	<i>e</i> -1478
32	22336	1	<i>e</i> -602	49	21367	5	<i>e</i> -1571
33	22320	2 (<i>d</i>)	<i>e</i> -618	50	21356	6	<i>e</i> -1582
34	22172	3 (<i>d</i>)	<i>e</i> -766	51	{21219 21204}	8 (<i>b</i>)	<i>e</i> -1719 } <i>e</i> -1726 <i>e</i> -1734 }
35	22141	6	<i>e</i> -797	52	20094	1 (<i>d</i>)	<i>e</i> -2844
36	22051	6	<i>e</i> -887	53	19984	4	<i>e</i> -2954
37	22027	5	<i>e</i> -911	54	19817	4	<i>e</i> -3121
38	22016	8	<i>e</i> -922	55	19784	2 (<i>d</i>)	<i>e</i> -3154
39	21919	6 (<i>d</i>)	<i>e</i> -1019				
40	21858	6 (<i>d</i>)	<i>e</i> -1080 (<i>k</i> -2847)				

$\Delta\nu$: 170 (*2dd*); 233 (*5bb*); 335 ($\frac{1}{2}$); 395 (4); 493 (3); 602 (1); 618 (*2d*); 770 (3*d*); 798 (6); 888 (6); 911 (5); 922 (8); 1019 (6*d*); 1081 (6*d*); 1122 (5*b, d*); 1172 (4*b, d*); 1236 (5); 1307 (4); 1390 (8*b*); 1478 (10*bb*); 1572 (5); 1583 (6); 1726 (8*bb*); 2345 (1*d*); 2956 (5*b, d*); 3122 (4); 3155 (2*d*).

Table VII. Ethyl α -furoate, $C_4H_5O \cdot CO \cdot O \cdot C_2H_5$.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	24336	4	<i>q</i> -3052	10	23722	2	<i>k</i> -983
2	24325	3 (<i>d</i>)	<i>q</i> -3063	11	23714	8	<i>k</i> -991
3	24290	2 (<i>d</i>)	<i>p</i> -3063	12	23628	3 (<i>d</i>)	<i>k</i> -1080 (<i>i</i> -888)
4	24228	2 (<i>d</i>)	<i>p</i> -3125 (<i>q</i> -3160)	13	23582	3 (<i>d</i>)	<i>k</i> -1123 (<i>i</i> -934)
5	24098	3	<i>k</i> -607	14	23524	6	<i>k</i> -1181 (<i>i</i> -993)
6	23936	1	<i>k</i> -769	15	23474	1/2	<i>k</i> -1231
7	23839 ?	1/2	<i>k</i> -866	16	23340	1	<i>i</i> -1176
8	23817	1	<i>k</i> -888	17	23319	3	<i>k</i> -1386
9	23778	3	<i>k</i> -927				

Table VII.—(Concluded)

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
18	23304	2	<i>k</i> -1401	39	21760	6 (<i>d</i>)	<i>e</i> -1178 (<i>k</i> -2945)
19	23228	6 (<i>b</i>)	<i>k</i> -1477	40	21725	1/2	<i>k</i> -2980
20	23134	1	<i>k</i> -1571	41	21706	2	<i>e</i> -1232
21	23123	4 (<i>b</i>)	(<i>i</i> -1382)	42	21654	6 (<i>d</i>)	<i>k</i> -3051
22	23100	3 (<i>d</i>)	<i>k</i> -1582	43	21642	8	<i>k</i> -3063
23	22730	3 (<i>b</i> , <i>d</i>)	<i>k</i> -1605	44	21582	3 (<i>d</i>)	<i>k</i> -3123
24	22585	3	<i>e</i> -208	45	21552	6	<i>e</i> -1386
25	22433	1	<i>e</i> -353	46	21541	3	<i>k</i> -3164
26	22332	6	<i>e</i> -505	47	21521	3	<i>k</i> -3184
27	22251	1/2	<i>e</i> -606	48	21488	1/2	<i>e</i> -1450
28	22176	3 (<i>d</i>)	<i>e</i> -687	49	21464	8 (<i>b</i>)	<i>e</i> -1474
29	22088	4	<i>e</i> -762	50	21367	1	<i>e</i> -1571 (<i>i</i> -3149)
30	22078	4	<i>e</i> -850	51	21355	6 (<i>d</i>)	<i>e</i> -1583
31	22051	4	<i>e</i> -860	52	21333	5	<i>e</i> -1605
32	22009	5	(<i>f</i> -917)	53	21224	8	<i>e</i> -1714
33	21956	2	<i>e</i> -887	54	21207	8	<i>e</i> -1731
34	21944	10	<i>e</i> -929	55	20011	1/2	<i>e</i> -2927
35	21921	1 (<i>d</i>)	<i>e</i> -983	56	19993	1	<i>e</i> -2945
36	21859	5	<i>e</i> -994	57	19889	3	<i>e</i> -3049
37	21815	4 (<i>b</i> , <i>d</i>)	<i>e</i> -1017	58	19874	6	<i>e</i> -3064
38	21780	1 (<i>d</i>)	<i>e</i> -1079	59	19816	1	<i>e</i> -3122
			<i>k</i> -1123				
			<i>k</i> -2925				

Benzene: 606 (6); (687) (1/2); 850 (4); 983 (2); 993 (10); 1179 (5); (1401) (2); 1583 (6*d*); 1605 (5); 2945 (1); 3051 (6*d*); 3063 (8); 3164 (3); 3184 (3).

Ethyl α -furoate: 208 (3, *b*, *d*); 353 (3); 505 (1); 606 (?); 765 (3*d*); 860 (4); 887 (4). 928 (5); 1017 (1*d*); 1079 (5); 1123 (4, *b*, *d*); 1179 (?); 1232 (2); 1386 (6); (1401) (2)?; 1450 (1/2); 1476 (8*b*); 1571 (1); 1583 (6*d*); 1714 (8); 1731 (8); 2926 (1*d*); 2980 (1/2); 3123 (3*d*).

Table VIII. α -Furfuracrylic acid, C₄H₃O·CH:CH·CO·OH.
(in alcohol).

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	24069	0 (<i>d</i>)	<i>k</i> -636	6	23682	3	<i>k</i> -1023
2	23994	1 (<i>d</i>)	<i>k</i> -711	7	23622	1/2 (<i>d</i>)	<i>k</i> -1083
3	23930	2	<i>k</i> -775	8	23551	1/2 (<i>b</i> , <i>d</i>)	<i>k</i> -1154
4	23818	2	<i>k</i> -887	9	23430	2 (<i>b</i>)	<i>k</i> -1275
5	23736	1/2	<i>k</i> -697	10	23309	4	<i>k</i> -1396

Table VIII.—(Concluded)

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
11	23220	6	<i>k</i> -1485	24	21733	4	<i>k</i> -2972
12	23127	2(<i>d</i>)	<i>k</i> -1678 (<i>i</i> -1389)	25	21655	4(<i>d</i>)	<i>e</i> -1283
13	23063	6(<i>d</i>)	<i>k</i> -1642	26	21585	1	<i>k</i> -3120
14	22312	1/2	<i>e</i> -626	27	21551	5	<i>e</i> -1387
15	22169	1(<i>d</i>)	<i>e</i> -769	28	21486	1	<i>e</i> -1452
16	22089	0	<i>e</i> -849	29	21456	8	<i>e</i> -1482
17	22057	5	<i>e</i> -881	30	21363	1	<i>e</i> -1575
18	21974	1/2	<i>e</i> -964	31	21297	10	<i>e</i> -1641
19	21917	5	<i>e</i> -1021	32	21254	2(<i>d</i>)	<i>e</i> -1684
20	21886	1/2(<i>d</i>)	<i>e</i> -1052	33	20060	2	<i>e</i> -2878
21	21853	1(<i>d</i>)	<i>e</i> -1085	34	20015	3	<i>e</i> -2923
22	21825	3(<i>d</i>)	<i>k</i> -2880	35	19967	3	<i>e</i> -2971
23	21781	5(<i>d</i>)	<i>e</i> -1157 (<i>k</i> -2924)	36	19815	1/2	<i>e</i> -3123

Alcohol: 849 (0); 884 (5); 1052 (1/2*d*); 1084 (1*d*); 1159 (5*d*); 1279 (4*d*); 1452 (1); 2879 (3*d*); 2924 (5*d*); 2972 (4).

α -Furfuracrylic acid: 631 (1/2*d*)?; (711) (1/2*d*)?; 772 (1*d*); 884 (5); 962 (1/2); 1022 (5); 1084; (1*d*); 1156 (5*d*); 1392 (5); 1483 (8); 1577 (2*d*); 1641 (10); 1634 (2*d*); 3121 (1).

Table IX. Ethyl α -furfuracrylate, C₄H₈O·CH:CH·CO·O·C₂H₅.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	23684	3	<i>k</i> -1021	14	22303?	0(<i>d</i>)	<i>e</i> -635
2	23622	1/2(<i>d</i>)	<i>k</i> -1083	15	22170	2	<i>e</i> -768
3	23544	1(<i>d</i>)	<i>k</i> -1161	16	22144	2	<i>e</i> -794
4	23492	2	<i>k</i> -1213	17	22076	1/2	<i>e</i> -862
5	23441	2	<i>k</i> -1264	18	22051	3	<i>e</i> -887
6	23421	3	<i>k</i> -1284	19	21999	1	<i>e</i> -939
7	23309	5	<i>k</i> -1396	20	21917	8	<i>e</i> -1021
8	23225	8	<i>k</i> -1480	21	21857	4	<i>e</i> -1081
9	23127	1	<i>h</i> -1578	22	21778	5(<i>d</i>)	<i>e</i> -1160
10	23061	8	<i>k</i> -1644	23	22726	5	<i>e</i> -1212
11	22873	4	<i>i</i> -1643	24	21673	5	<i>e</i> -1265
12	22806	1/2(<i>d</i>)	<i>i</i> -1710	25	21655	8	<i>e</i> -1283
13	22476	1/2	<i>e</i> -462	26	21577	1	<i>e</i> -3128

Table IX.—(Concluded)

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
27	21549	9	<i>e</i> -1389 (<i>k</i> -3156)	32	20010	1 (<i>d</i>)	<i>e</i> -2928
28	21460	10	<i>e</i> -1478	33	19965	2	<i>e</i> -2973
29	21367	4	<i>e</i> -1571	34	19900	5	<i>e</i> -3038
30	21298	10	<i>e</i> -1640	35	19817	2	<i>e</i> -3121
31	21234	8 (<i>d</i>)	<i>e</i> -1704	36	19787	1 (<i>d</i>)	<i>e</i> 3151

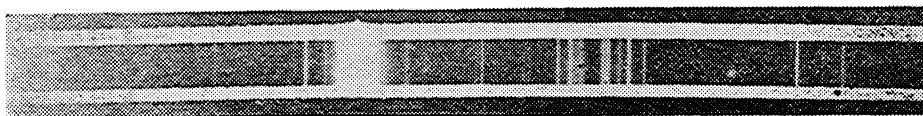
$\Delta\nu$: 462 (¹/₂); 635 (0*d*)?; 768 (2); 794 (2); 862 (¹/₂); 887 (3); 939 (1); 1021 (8); 1081 (4); 1160 (5*d*); 1212 (6); 1265 (5); 1283 (8); 1392 (9); 1479 (10); 1575 (4); 1640 (10); 1704 (8*b*, *d*); 2926 (1*d*); 2976 (2); 3035 (5); 3125 (2); 3154 (1).

Table X.

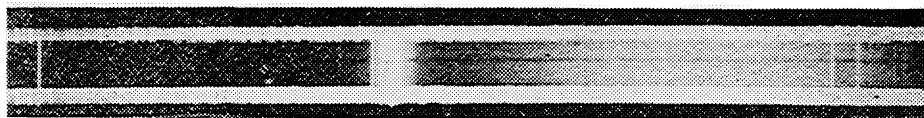
Tetrahydro- α -furfuryl alcohol, C₄H₇O·CH₂·OH.

No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$	No.	ν (cm. ⁻¹)	<i>I</i>	$\nu_0 - \Delta\nu$
1	23783	4 (<i>d</i>)	<i>k</i> -922	9	21931	2 (<i>d</i>)	<i>k</i> -2774
2	23576	¹ / ₂ (<i>d</i>)	<i>k</i> -1129	10	21821	6 (<i>d</i>)	<i>e</i> -1117
3	23251	3 (<i>d</i>)	<i>k</i> -1454	11	{ 21759	4 (<i>b</i> , <i>d</i>)	{ <i>k</i> -2946
4	22787	2 (<i>d</i>)	<i>e</i> -151	12	{ 21728	4 (<i>b</i> , <i>d</i>)	{ <i>k</i> -2978
5	22766	1 (<i>d</i>)	<i>e</i> -172	13	21488	4	<i>e</i> -1450
6	22121	3 (<i>b</i> , <i>d</i>)	<i>e</i> -817	14	21451	3	<i>e</i> -1487
7	22062?	¹ / ₂ (<i>b</i> , <i>d</i>)	?	15	20000		<i>e</i> -2938
8	22023	6 (<i>d</i>)	<i>e</i> -915	16	19958	3 (<i>b</i>)	<i>e</i> -2980

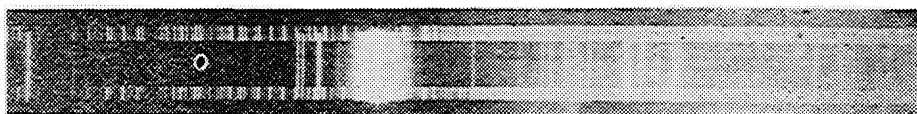
$\Delta\nu$: 151 (2*d*); 172 (1*d*); 817 (3*b*, *d*); 918 (6*d*); 1123 (6*d*); 1452 (4*d*); 1487 (3*d*); (2774) (2*d*); 2942-2979 (4*b*, *d*).

 α -Methyl-furan C₄H₃O·CH₃ α -Furfuryl alcohol C₄H₃O·CH₂·OH

α -Furfuryl acetate $C_4H_3O \cdot CH_2 \cdot O \cdot OC \cdot CH_3$



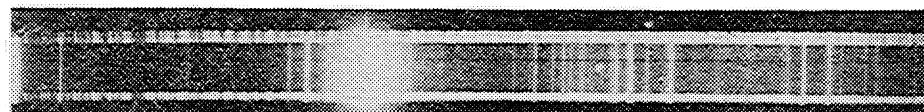
α -Furfural $C_4H_3O \cdot CO \cdot H$



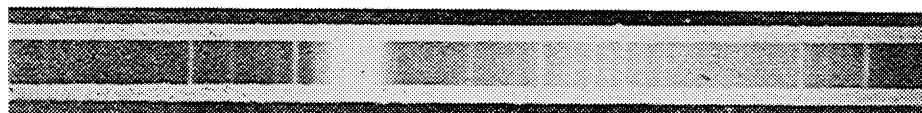
α -Furoyl chloride $C_4H_3O \cdot CO \cdot Cl$



Methyl α -furoate $C_4H_3O \cdot CO \cdot O \cdot CH_3$



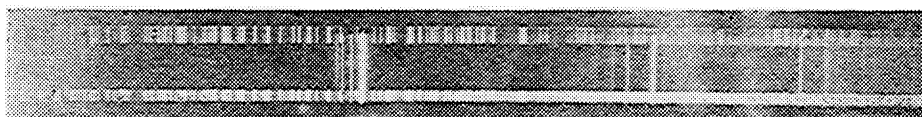
Ethyl α -furoate $C_4H_3O \cdot CO \cdot O \cdot C_2H_5$ (in benzene)



α -Furfuracrylic acid $C_4H_3O \cdot CH : CH \cdot CO \cdot OH$ (in alcohol)



Ethyl α -furfuracrylate $C_4H_3O \cdot CH : CH \cdot CO \cdot O \cdot C_2H_5$



Tetrahydro- α -furfuryl alcohol $C_4H_7O \cdot CH_2 \cdot OH$



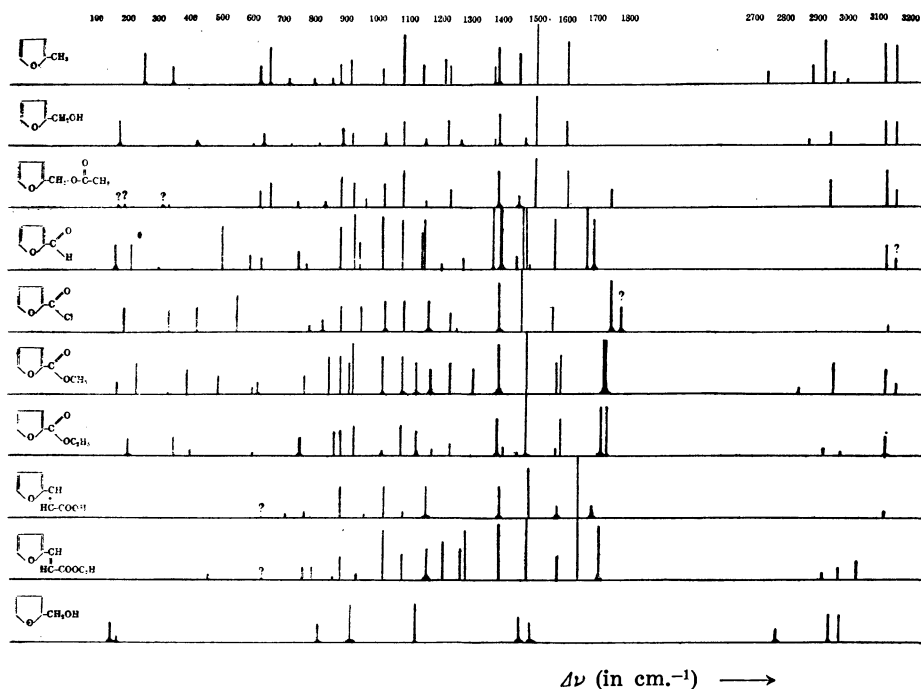
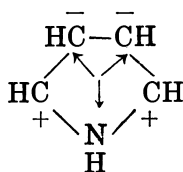


Fig. 1.



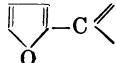
The frequency of 1530 cm^{-1} is only observed in the case of α -derivatives of pyrrole. In the case of α -derivatives of furan, however, the intense lines corresponding to the frequency of 1460 and 1507 cm^{-1} are observed. The frequency of $\Delta\nu$, 1460 cm^{-1} , is found also in furfural and furoyl chloride which do not possess $-\text{CH}_2-$ group in their molecules. The frequency of $\Delta\nu$, 1450 cm^{-1} , is generally considered as due to the transversal vibration of the $-\text{CH}_2-$ group. In the case of methyl α -furoate, ethyl α -furoate, α -furfuracrylic acid, and its ethyl ester, the frequency of 1478 cm^{-1} is observed. The frequency of 1460 cm^{-1} in furoyl chloride, those of 1463

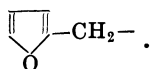
and 1476 cm.^{-1} in furfural are observed. It is better not to attribute these frequencies in furan derivatives to the transversal vibration of the CH_2 -group, for CH_2 -group is not found in α -furoyl chloride and furfural molecules. So these frequencies in question and that of 1507 cm.^{-1} in α -methyl-furan, α -furfuryl alcohol, and α -furfuryl acetate are considered as associated with the furan ring. Geo. Glockler and B. Wiener⁽¹³⁾ have reported quite recently that the frequencies of 624, 758, 878, 1021, 1078, 1156, 1378, and 1467 cm.^{-1} are due to the furan ring and 1567 cm.^{-1} is attributed to the $\text{C}=\text{C}$ bond. From the fact that the frequency of 1607 cm.^{-1} is found in α -methyl-furan, α -furfuryl alcohol, and α -furfuryl acetate, the formula with double bonds, instead of the centric formula, is supported by the present investigation, since the frequency of 1607 cm.^{-1} is generally accepted as due to the vibration of $-\text{C}:\text{C}-$. If we take the frequency of 1572 cm.^{-1} in methyl α -furoate, ethyl α -furoate, and ethyl α -furfuracrylate, and the frequency of 1563 cm.^{-1} in furfural and α -furoyl chloride, as corresponding to the frequency of 1607 cm.^{-1} in α -methyl-furan, etc., it seems that the formula with double-bonds is more probable than the centric formula for the furan ring, at least, in α -derivatives. The further discussion will be reported after studying the Raman spectra of furan itself, its β and other derivatives, which are now in the course of experiments.

Summary.

(1) The Raman spectra of the following substances have been measured: α -methyl-furan, α -furfuryl alcohol, α -furfuryl acetate, furfural, α -furoyl chloride, methyl α -furoate, ethyl α -furoate, α -furfuracrylic acid, ethyl α -furfuracrylate, and tetrahydro- α -furfuryl alcohol.

(2) The frequencies of $\Delta\nu$, 625 (or 650), 888, 925, 1021, 1081, 1153, 1232, 1390, 1460 (or 1480), 1507, 1575 (or 1605), 3122, 3153 cm.^{-1} , are observed as the characteristic lines of the α -mono-derivatives of furan.

(3) The frequencies of $\Delta\nu$, 1460 (or 1480) and 1572 cm.^{-1} , are observed in the type of , while those of 1507 and 1605 cm.^{-1} in the type of



(13) G. Glockler and B. Wiener, *J. Chem. Phys.*, **2** (1934), 47.

(4) It is shown that the investigation supports the formula with double bonds in the case of α -mono-derivatives of furan.

The authors express their thanks to Ass. Prof. T. Nozoe for his kind help and advice in the work of synthesis of the materials.

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THE COLLOIDAL BEHAVIOUR OF SERICIN. IV.*

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Sec. XII. The Colour Reactions of the Sericin Solution.

For the aqueous solution of sericin the biuret, xanthoproteic, and Millon's reactions have been long known.

(1) **The Biuret Reaction.** This reaction of sericin was completely investigated by R. Inoue⁽⁴¹⁾. He applied it for the determination of "kaijo" of cocoons, because the tinge of colour produced in the biuret reaction varied with the "kaijo" of cocoons.

(2) **The Yellow Colouration.** An almost colourless or a slightly yellowish solution is obtained when the white cocoon layer is boiled with water. M. Oku⁽⁴²⁾ investigated the colouring matters of the cocoon layer and showed the existence of a flavone-like glucoside in its alcoholic extract. As the colourless glucoside gives yellow colour by hydrolysis, the colour of the aqueous solution of the cocoon layer may be produced partly by the hydrolysis of this substance during the boiling of cocoons in water. And this yellow colouration was also produced by the addition of alkaline substances (NaOH, ammonia, etc.) to a cold aqueous solution of sericin. But we can easily get the yellow colouration by adding a small solid mass of quick lime to a sericin

* Continued from p. 302 of this volume.

(41) R. Inoue, *Bull. Seric. and Silk Ind. Japan*, **3** (1931), 171.

(42) M. Oku, *J. Agri. Chem. Soc. Japan*, **6** (1930), 1103.

solution. The aqueous or alcoholic solution obtained from the cocoon having good "kaijo" showed generally lighter colouration than the one having bad "kaijo". By adding quick lime to an alcoholic solution of glycocoll a similar beautiful colouration resulted, but its colour turned to violettish gray in about ten hours at room temperature.

(3) **Engel's Colour Reaction.** E. Hiratsuka⁽⁴³⁾ showed that amino-acids and other nitrogen compounds existed in the silk gland, and also R. Inoue noticed that in the sericin solution there was a free or a loosely combined amino-acid giving a weak ninhydrine reaction.

The characteristic blue colour reaction of the glycocoll solution with phenol and sodium hypochlorite solutions was found by Engel and is called Engel's reaction. As shown by O. Früth⁽⁴⁴⁾ the blue colouration is given not only by glycocoll, but by many other substances like ammonium salts and biuret. Glycocoll, however, gives the deepest blue colour which is stable during a few days. The alcoholic solution of sericin also gave Engel's reaction, but the colour was rich in greenish tinge like that given by ammonium salts. The difference in depth of colour was hardly recognized with the difference in "kaijo", though bad "kaijo" was apt to show somewhat deeper colour. From these results it can be seen that the blue colouration given by the alcoholic solution of sericin is similar to those given by solutions of glycocoll, aspartic acid, and ammonium oxalate, which give all violet fluorescence under ultra-violet rays. As it was mentioned in the introduction, R. Inoue observed that glycocoll and aspartic acid were contained in a large amount in the sericin from the inner layer of cocoons.

(4) **Markris' Colour Reaction.** Markris (1931)⁽⁴⁵⁾ detected a minute quantity of ammonia by using a 5 per cent. solution of tannin and a 20 per cent. solution of silver nitrate. When this reaction was carried out with an alcoholic solution of cocoon layer, a very slightly whitish turbidity took place first, and then slightly brownish dark yellow colour followed in five minutes. But the development of the colour was not so quick as in the case of free ammonia.

(5) **Colour Reaction with Concentrated Sulphuric Acid.** When 0.5 c.c. of an alcoholic solution of sericin, after adding three drops of a 3 per cent. alcoholic solution of α -naphthol, was thoroughly mixed with 5 c.c. of cold 75 per cent. sulphuric acid, a yellowish green colouration took place. If a

(43) E. Hiratsuka, loc. cit.

(44) O. Früth, *Biochem. Z.*, **240** (1931), 56-61.

(45) Markris, *Z. anal. Chem.*, **84** (1931), 241-242.

carbohydrate were present in solution, violettish red or red colouration would develop as modified Molisch reaction. Glycocoll and ammonium oxalate gave a colouration similar to that of sericin.

(6) **Arginine Colour Reaction.** When two drops of a 0.1 per cent. alcoholic solution of α -naphthol and a few drops of a 5 per cent. sodium hypochlorite were added to 3 c.c. of a sericin solution, a deep brownish red colouration took place. The sericin solution obtained from cocoons of good "kaijo" gave more intense colour than that from cocoons of bad "kaijo". From these results it is probable that flavone-like compounds, free amino-acids like glycocoll and aspartic acid, and ammonium salts like ammonium carbonate and oxalate, are contained in a very minute quantities in the aqueous solution of sericin obtained by boiling cocoon layers in water for 30 minutes, and that the solubility of sericin in water depends partly on the basic groups like arginine-group which have intimate relation with water molecules.

Sec. XIII. The Gold Number of the Sericin Solution.

The protection of less stable sols by organic sols was first definitely recognized by E. von Mayer and Lottermoser in 1897. Lottermoser reached the conclusion that on addition of a very stable colloid, such as albumin, gelatin, and gum arabic, to a silver sol, no precipitation is caused by electrolytes before the stable colloid is gelatinized. The degree of protection is expressed by the "gold number", that is the weight in mg. of a

Table 66.

Colloid	Gold number
Gelatin	0.005-0.01
Casein (in ammonia)	0.01
Egg-albumin	0.15-0.25
Gum arabic	0.15-0.25, 0.5-4.0

colloid which just fails to prevent the change from red to violet when 1 c.c. of a 10 per cent. solution of sodium chloride is added to 10 c.c. of a gold sol (0.0053-0.0058 percent.). Some examples are quoted from Zsigmondy's table in Table 66.

K. Yamamoto (1929)⁽⁴⁶⁾ investigated the protective action of sericin precipitated by alcohol and observed that the gold number of sericin was approximately equal to that of gelatin. He also noticed that the protective action of sericin obtained from inner layer of cocoons was less than that of sericin obtained from outer layer.

From many investigations we can reach the conclusion that the stability of colloid particles depends mainly on the chemical factor conditioned by the

(46) K. Yamamoto, *Reports Gunze Phys. Chem. Lab. Japan*, **4** (1929), 23-27.

constitution of colloid particles and on the electrostatical factor conditioned by adsorption and hydration.

S. Liepatoff (1930) considered that the stability of colloidal particles depends on their charges and the degree of saturation of their surfaces. To the protective action of colloids, C. Marie and N. Marinesco (1931) gave an explanation that the colloid particle is covered with the polarized protecting body and becomes similar to the latter in its behaviour.⁽⁴⁷⁾

The data obtained are given in Table 67. From my results it can be seen that the gold number of sericin is nearly equal to that of egg-globulin (0.02–0.05), gelatin (0.007–0.06), and amorphous albumin (0.03–0.06), and that it depends on the concentration of sericin and also on the “kaijo” of cocoons at the constant pH value and temperature.

Table 67. Effect of concentration on the gold number of sericin (at 30°C.).

Good “kaijo”		Mid. “kaijo”		Bad “kaijo”	
Conc. (%)	Gold numb.	Conc. (%)	Gold numb.	Conc. (%)	Gold numb.
0.075	0.03	0.095	0.0285	0.07	0.0385
0.10	0.03	0.10	0.03	0.125	0.0312
0.12	0.027	0.15	0.03	0.15	0.030
0.20	0.020	0.21	0.021	0.23	0.023
0.21	0.021	—	—	—	—

(1) Effect of pH. The gold number of sericin is maximum at the isoelectric point as shown by Fig. 27.

Table 68.

“Kaijo”	pH giving maximum gold number
Good	4.20
Middle	4.25
Bad	4.30

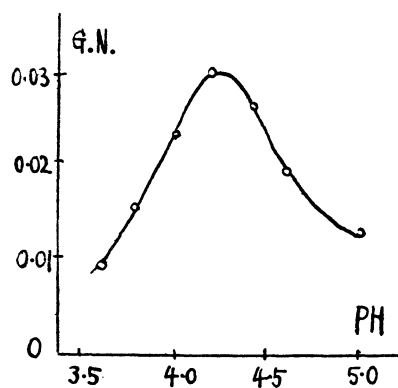


Fig. 27.

(47) C. Marie and N. Marinesco, *Compt. rend.*, **192** (1931), 92–94.

(2) **Effect of Temperature.** As already stated, the aggregation of sericin micellæ varies with temperature, so its protective action must be raised with it. Above 60°C. sericin particles exist in sol-form, and the protective power increases remarkably as shown in Table 69 and in Fig. 28.

Table 69. Effect of temperature on gold number.

Temp. (C.)	Good	Mid.	Bad
	0.1%	0.11%	0.085%
0	0.030	0.033	0.0375
20	0.03	0.0325	0.0375
40	0.025	0.028	0.030
60	0.012	0.019	0.0243
80	0.01	0.016	0.0215

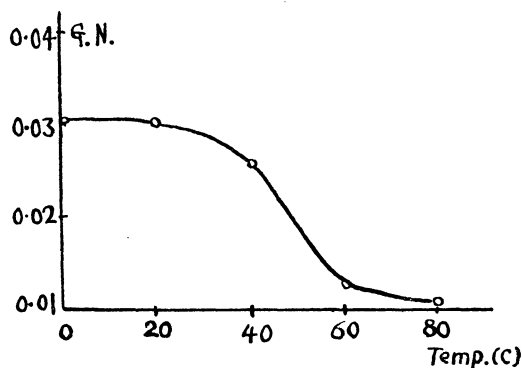


Fig. 28.

(3) **Effect of Aging.** The gold number of sericin increased on aging the solution, probably because the sericin particles formed larger aggregates of less protective power.

Sec. XIV. The Protective Actions of the Sericin Solution.

(1) **The Emulsifying Properties of the Sericin Systems.** When a liquid immiscible with water is shaken with an aqueous solution of sericin, a very stable emulsion results. On standing for a few days the emulsion creams in a separate layer. In the following experiments each emulsion was made with 5 c.c. of a sericin solution and 10 c.c. of an immiscible liquid in a test-tube with a diameter 2 cm. . Such test-tubes were stoppered and shaken by a shaking machine for half an hour, and then, after giving two hundred shakes by hand, they were set aside. The volume of stable emulsions was read from time to time.

(a) **Effect of Concentration of Sericin.** First I investigated how the emulsifying properties vary with the sericin content. Experiments were carried out by mixing the sericin solutions (0.08–0.8%) with various liquids in the manner described above. The results are given in Table 70, where the emulsifying power is expressed by the formula $\frac{V-v}{V} \times 100$, V being the initial volume of emulsion (15 c.c.), and v the volume of aqueous layer separated from the emulsion after a definite time.

Table 70. Benzene and good "kaijo."

Conc. of sericin (%)	Emulsifying power			
	10 min.	30 min.	60 min.	120 min.
0.802	98.87	97.73	97.16	96.59
0.65	100.0	99.14	97.99	97.65
0.484	100.0	99.95	99.92	99.89
0.32	100.0	100.0	100.0	100.0
0.26	100.0	100.0	100.0	100.0
0.084	100.0	98.13	96.25	96.25

At the low concentrations (from 0.25 to 0.35 per cent.) the emulsifying power of the sericin solution was strongest and it diminished gradually with time, following a monomolecular reaction. After two hours there was no remarkable change in it.

These results are expressed in Fig. 29. Sericin had a maximum emulsifying power for liquids examined and the position of the maximum seems to depend on their dielectric constants (Table 71).

Table 71. The emulsifying powers of various sericin systems.

Conc. (%)	CCl_4	CHCl_3	Poupa oil	Olive oil
0.802	92.14	95.51	74.11	85.12
0.65	90.74	94.12	84.78	94.12
0.48	89.79	93.34	87.22	100.0
0.32	86.52	92.14	92.53	100.0
0.26	85.39	90.76	93.01	96.25
0.08	73.52	87.94	97.50	93.34

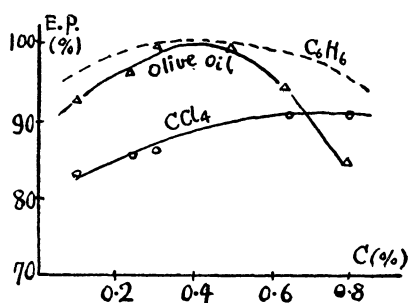


Fig. 29.

At the constant concentration, sericin obtained from cocoons having good "kaijo" had a greater emulsifying power than that obtained from cocoon having bad "kaijo". This may be due to the difference in adsorption of sericin particles on the interface of liquid particles. Pupa oil manifested a reverse relation.

(b) **The Adsorption of Sericin on the Interface.** In order to determine the extent of adsorption of sericin on the interface of the emulsion, analyses of the aqueous phase before emulsification were compared with those of the first few c.c. of the aqueous phase that

separated from the emulsion. The micro-Kjeldahl-method for determination of nitrogen in proteins was used to determine the sericin content. The results are shown in Table 72.

Table 72.
Nitrogen content in mg. per c.c. (For good "kaijo").

Original solution	Benzene			Chloroform		
	Separated solution	Difference	Emuls. power	Separated solution	Difference	Emuls. power
1.290	1.213	0.077	96	1.135	0.155	95
1.071	0.976	0.095	97	0.937	0.134	94
0.785	0.626	0.159	99.9	0.665	0.120	93
0.528	—	—	—	0.455	0.073	92
0.428	—	—	—	0.357	0.071	90
0.143	0.075	0.068	96	0.107	0.036	87

It can be seen that sericin was taken from the aqueous phase and concentrated on the interface of the emulsion, and that oil particles were stabilized by the accumulation of sericin particles on their interfaces.

(c) Effect of *pH*. The emulsifying power of sericin depends further on the hydrogen-ion concentration of the medium, for the state of aggregation of sericin is remarkably influenced by the *pH* value.

Fig. 30, showing the influence of *pH* on emulsifying property of the sericin solution, shows that, if *pH* of the sericin solution is near the isoelectric point, the least stable emulsion is formed. The *pH* values corresponding to the minimum emulsifying power are given in Table 73.

Table 73.

"Kaijo"	C ₆ H ₆ -H ₂ O emuls.	Pupa oil-H ₂ O emuls.
Good	<i>pH</i> 4.0	<i>pH</i> 4.3
Middle	4.5	4.6
Bad	4.8	4.8

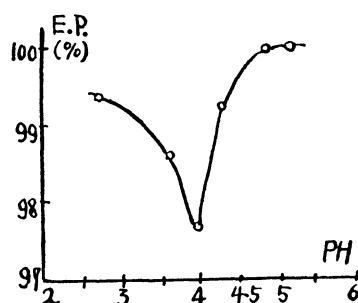


Fig. 30.

In the cases of CCl₄, CHCl₃, C₆H₆, and aniline the same results were obtained, but benzene did not produce an emulsion at the more acid side

than pH 3.5. Change of pH of the sericin solution affects its emulsifying properties in a manner closely related to the effect of change of pH on the surface tension and viscosity of the sericin solution.

(2) **The Protective Action of Sericin against the Oxidation of Pyrogallol in the Presence of the Purpureo-salt.** With Prof. Y. Shibata I investigated the oxidase-like action of complex cobalt salts, and found that the aqueous solution of pyrogallol was catalytically oxidized in the presence of the purpureo-salt, pentammine cobalt chloride, even in a very small concentration and it became gradually brownish yellow.⁽⁴⁸⁾

Taking the colour as expressing the degree of oxidation, the colour developed in 15 minutes in a number of solutions, prepared by adding 0.1 c.c. of a 10 mg. mol. solution of purpureo-salt to 10 c.c. of a 1 mg. mol.

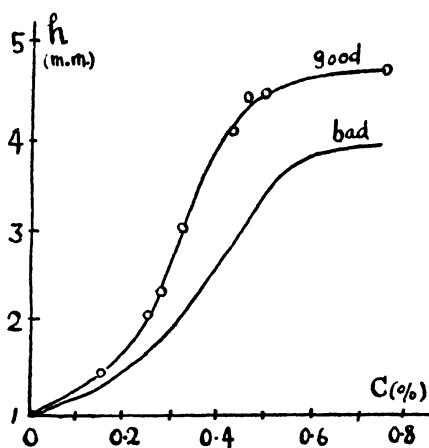


Fig. 31.

solution of pyrogallol with the addition of sericin in various concentrations, were compared by a colorimeter with that of a standard solution prepared similarly but without sericin. Sericin protected pyrogallol from oxidation catalysed by the purpureo-salt, the height (h in Fig. 31) of the solution at the colorimeter increasing with increasing concentration of sericin. The sericin solution obtained from cocoons of good "kaijo" had stronger protective power than that obtained from

cocoons of bad "kaijo", as in the case of the gold number of sericin.

(3) **The Protective Action of Sericin against the Decomposition of Hydrogen Peroxide in the Presence of Platinum Sol.** It was early recognized by Groth that gelatin possesses a power to protect hydrogen peroxide from decomposition catalysed by platinum sol. Sericin showed a protective action against the decomposition of hydrogen peroxide (Fig. 32).

As it is well known, the decomposition of hydrogen peroxide in the presence of platinum sol is a mono-molecular reaction expressed by

$$K = \frac{2.303}{t} \cdot \log \frac{a}{a-x},$$

(48) Y. Shibata and H. Kaneko, *J. Chem. Soc. Japan*, **44** (1922), 833-884.

Table 74. Reaction velocity constant, $K \times 10^3$.

t (min.)	Volume of sericin added (c.c.)			
	0	0.1	0.5	0.7
0	—	—	—	—
5	30.24	(24.40)	(15.85)	(12.42)
10	30.33	(26.43)	(17.48)	(17.61)
15	31.67	27.16	25.00	19.09
20	32.29	28.51	25.07	18.30
25	33.83	29.74	24.84	19.13
30	33.19	30.50	24.00	20.70
60	32.96	30.25	24.93	20.74
mean	32.07	29.23	24.77	19.59

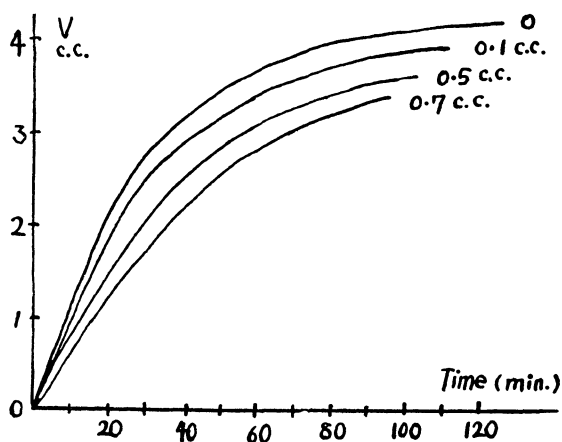


Fig. 32.

where K is the reaction velocity constant, x and α are the quantities of oxygen evolved at time t and at infinite time t_{∞} respectively.

The reaction velocity constant was found to be reduced by the addition of sericin as shown in Table 74. The velocity constant K was inversely proportional to the concentration of sericin in low concentration.

Table 75. Effect of aging.

Pt-sol, 0.5 c.c. ; sericin, 0.5 c.c.

Time of aging (min.)	Good "kaijo"			Bad "kaijo."	
	0.44%	0.43%	0.32%	0.42%	0.35%
0	1.40	1.53	2.22	1.81	2.28
40	1.59	1.63	2.41	2.11	2.52
90	1.70	1.80	2.50	2.13	2.65
120	1.62	1.71	2.38	1.98	2.45
180	1.25	1.38	1.97	1.52	2.01
240	0.81	0.85	1.55	1.00	1.58
300	—	0.67	—	—	—

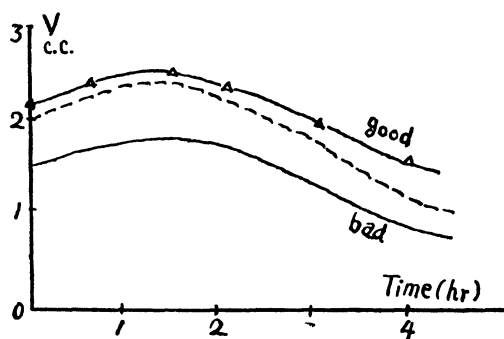


Fig. 33.

On aging the sericin sol at 13°C ., its protective action against the decomposition reached a minimum value (Table 75 and Fig. 33). Near this point, many physico-chemical properties of the sericin solution showed also remarkable changes.

(To be continued.)

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. V. THE ACTION ON METHYLCYCLOHEXANOLS AND MENTHOL.*

By Harushige INOUE.

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Cyclohexanol is easily dehydrated to cyclohexene by the contact action of alumina, silica, or other dehydrating agents, at about 300°. ⁽¹⁾ The conversion of cyclohexane derivatives into cyclopentane series, however, has been effected only by the action of the strong mineral acids such as hydriodic acid as Markonikoff ⁽²⁾ first observed, or only at higher temperatures as Ipatiew ⁽³⁾ reported. The present author ⁽⁴⁾ previously observed that when Japanese acid earth is used as a contact material, cyclohexanol is chiefly converted into methylcyclopentane at 350°, while at 250° it is mainly changed into cyclohexene. A similar isomerisation was also ascertained in the case of 1-methylcyclohexanol-(2).

The present experiment was undertaken to examine the relation between the position of the methyl group in methylcyclohexanols and the yield of each reaction product and further to study the catalytic action of the earth on menthol. The methylcyclohexanols used in the experiment were prepared by the hydrogenation of pure cresols. Their physical constants are shown in Table 1.

Table 1.

	B.p.	d_4^{20}	n_D^{20}
1-Methylcyclohexanol-(2)	167—170°	0.9473	1.45998
1-Methylcyclohexanol-(3)	173—176°	0.9300	1.45345
1-Methylcyclohexanol-(4)	172—174°	0.9320	1.46016

I. 1-Methylcyclohexanol-(3). By passing 70 g. of 1-methylcyclohexanol-(3) on the earth heated at 250°, 42.6 g. of oil (d_4^{20} , 0.8183) and 8.9 g.

* An epitomized translation of the paper published in Vol. 29 of the *Reports of the Tokyo Imperial Industrial Research Laboratory*.

(1) Ipatiew, *J. Russ. Phys. Chem. Soc.*, **38** (1906), 96; Sendrens, *Compt. rend.*, **144** (1907), 1110; Brunnel, *Bull. Soc. Chim.*, [3], **33** (1905), 270.

(2) *Ber.*, **30** (1897), 1226; *Ann.*, **307** (1899), 340.

(3) *J. Russ. Phys. Chem. Soc.*, **43** (1911), 1431.

(4) This Bulletin, **1** (1926), 219.

of water were obtained. The former, after subjected to fractional distillation ten times, gave the fractions shown in Table 2.

Table 2.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_a^{20}	n_p^{20}	n_T^{20}	Analysis (%)	
								C	H
92–95°	1.1	0.7800	0.7621	1.42090	1.41864	1.42646	1.43183	—	—
95–99°	2.2	0.7866	0.7691	1.42460	1.42230	1.43035	1.43521	85.85	14.01
99–102°	11.3	0.7909	0.7732	1.42790	1.42552	1.43368	1.43847	86.24	13.85
102–105°	8.5	0.7954	0.7787	1.43080	1.42859	1.43694	1.44164	86.45	13.55
105–110°	2.1	0.8024	0.7847	1.43482	1.43241	1.44105	1.44616	86.55	13.32
Residue	11.6	0.9342	0.9194	—	—	—	—	—	—
{ A B C	0.4	0.8836	0.8358	1.46375	—	—	—	—	—
	4.3	0.9256	0.9110	1.49758	—	—	—	—	—
	4.4	0.9634	0.9502	1.53174	—	—	—	—	—

The residue was further separated into three parts, A, B, and C, by fractional steam distillation as shown in the table.

The physical constants and results of elementary analyses of the fractions show that the main reaction product is methylcyclohexane, while in the case of 1-methylcyclohexanol-(2) methylcyclohexene is mainly produced under the same condition.⁽⁵⁾

When 1-methylcyclohexanol-(3) (150 g.) was treated similarly at 350°, 103.4 g. of oil (d_0^{20} , 0.8075) and 20.0 g. of water were obtained. The former gave the fractions shown in Table 3 after ten times fractional distillations.

Table 3.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_a^{20}	n_p^{20}	n_T^{20}	Analysis (%)	
								C	H
To 80°	1.3	0.7103	0.6901	1.39172	1.38973	1.39724	1.40280	84.25	15.75
80–90°	4.1	0.7643	0.7458	1.41192	1.40990	1.41756	1.42221	84.57	15.37
90–98°	5.6	0.7736	0.7571	1.41710	1.41492	1.42264	1.42725	85.25	14.86
3–96°	9.0	0.7787	0.7615	1.41970	1.41728	1.42538	1.42998	85.40	14.56
96–99°	13.5	0.7855	0.7685	1.42380	1.42149	1.42961	1.43434	85.72	14.32
99–102°	15.9	0.7940	0.7769	1.42920	1.42673	1.43526	1.44028	85.86	14.19

(5) Inoue, This Bulletin, **I** (1926), 219.

Table 3. (Concluded)

B.p.	Yield (g.)	d_4^{20}	d_4^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
102—105°	6.3	0.7997	0.7835	1.43367	1.43110	1.44001	1.44528	86.05	13.89
105—110°	3.6	0.8051	0.7896	1.43792	1.43535	1.44462	1.45048	86.67	13.34
110—115°	2.4	0.8129	0.7956	1.44301	1.44008	1.44993	1.45608	—	—
115—125°	2.8	0.8201	0.8038	1.44857	1.44551	1.45585	1.46199	—	—
125—140°	2.1	0.8378	0.8217	1.46105	1.45783	1.46940	—	—	—
Residue	25.1	0.9642	0.9506	—	—	—	—	—	—
{ A	0.9	0.8760	0.8606	1.48515	—	—	—	—	—
{ B	20.0	0.9603	0.9472	1.54432	—	—	—	—	—
{ C	2.6	—	—	—	—	—	—	—	—

The first fraction of Table 3 mainly consists of methylcyclopentane, as its physical constants and chemical composition clearly show. The fractions with higher boiling points are, in this case, chiefly composed of dimethylcyclopentane, ethylcyclopentane, methylcyclohexane, and a small amount of methylcyclohexenes. Δ^1 -Methylcyclohexene, which was confirmed to occur in the reaction product by the oxidation with nitric acid, yielding thereby adipic acid (m. p. 150°) and β -methyladipic acid (m. p. 88—90°), can not be considered to have been formed by the simple dehydration of 1-methylcyclohexanol-(3). It is probable that Δ^2 - or Δ^3 -methylcyclohexene, originated by the dehydration of 1-methylcyclohexanol-(3) re-arranges itself to Δ^1 -methylcyclohexene, the most stable form of the three isomers, by the contact action of the acid earth. The same experimental fact was observed by Wallach⁽⁶⁾ when 1-methylcyclohexanol-(3) was treated with zinc chloride and also by the present author and Ishimura⁽⁷⁾ when methylcyclohexylamines were treated with Japanese acid earth.

In order to get the more precise knowledge of the reaction products, the following experiment was performed.

1-Methylcyclohexanol-(3) (76.0 g.) was passed on the earth heated at 350° and 54.6 g. of oil (d_4^{20} , 0.8248) and 9.6 g. of water were obtained. The oily substance was treated with concentrated sulphuric acid to remove unsaturated hydrocarbons, and 30.9 g. of saturated hydrocarbons were left unaffected by the acid, which were then submitted to fractional distillation ten times, giving the fractions shown in Table 4.

(6) *Ber.* **35** (1902), 2823.

(7) To be reported in next paper.

Table 4.

B.p.	Yield (g.)	d_0^{20}	d_0^{20}	n_D^{20}	n_g^{20}	n_p^{20}	n_l^{20}	Analysis (%)	
								C	H
To 86°	0.9	0.7347	0.7169	1.40059	1.39383	1.40550	1.41021	—	—
85—89°	2.8	0.7611	0.7438	1.41153	1.40841	1.41659	1.41992	86.16	14.81
89—92°	—	0.7695	0.7522	1.41381	1.41171	1.41903	1.42326	86.30	14.69
92—95°	2.9	0.7720	0.7551	1.41525	1.41311	1.42038	1.42470	85.53	14.50
95—98°	8.9	0.7769	0.7602	1.41340	1.41562	1.42322	1.42763	86.72	14.28
98—101°	2.3	0.7804	0.7641	1.42000	1.41783	1.42528	1.42970	86.91	14.12
101—105°	1.0	0.7835	0.7672	1.42165	1.41944	1.42686	1.43134	86.24	13.80
Above 105°	0.7	0.7977	0.7816	1.42330	1.42708	1.43467	1.43925	—	—
Residue	6.3	0.9091	0.8957	1.49412	—	—	—	—	—

As is seen in Table 4, the third fraction boiling between 89° and 92° is noticed to consist mainly of dimethylcyclopentane from its physical constants and the result of elementary analysis, whereas the sixth fraction boiling between 98° and 101° is almost pure ethylcyclopentane.

II. 1-Methylcyclohexanol(4) By passing 70.0 g. of 1-methylcyclohexanol(4) on the earth heated at 250°, 42.0 g. of oil (d_0^{20} , 0.8112) and 9.8 g. of water were obtained. The former, after ten times fractional distillations, gave the fractions shown in Table 5.

Table 5.

B.p.	Yield (g.)	d ₀ ⁰	d ₀ ²⁰	n _D ²⁰	n _v ²⁰	n _p ²⁰	n _t ²⁰	Analysis (%)	
								C	H
98—96°	0.8	0.7746	0.7571	1.41900	1.41673	1.42450	1.42960	—	—
96—99°	3.6	0.7853	0.7693	1.42410	1.42185	1.42981	1.43454	85.20	14.82
99—102°	12.6	0.7927	0.7752	1.42830	1.42587	1.43407	1.43881	86.18	13.84
102—105°	7.0	0.7985	0.7823	1.43281	1.43030	1.43892	1.44420	86.30	13.67
105—110°	1.3	0.8065	0.7894	1.43803	1.43545	1.44745	1.45019	86.73	13.35
110—115°	0.9	0.8169	0.7997	1.44426	1.44149	1.45102	1.45707	—	—
Residue	11.8	0.9412	0.8737	1.51723	—	—	—	—	—
A B C	1.5	0.9302	0.9164	1.50126	1.49767	1.51008	—	—	—
	4.5	0.9373	0.9220	1.51098	1.50711	1.52010	—	—	—
	4.9	0.9793	0.9664	1.54760	—	—	—	—	—

The residue was further separated by fractional steam distillation into three parts, A, B, and C.

The numerical data of Table 5 tell us that almost the same reaction took place as in the case of 1-methylcyclohexanol-(3) (cf. Table 2).

When 1-methylcyclohexanol-(4) (150.0 g.) was passed on the earth heated at 350°, 111.5 g. of oil (d_0^{20} , 0.8141) and 20.4 g. of water were obtained, and the former was divided into fifteen portions by ten times fractional distillations (Table 6).

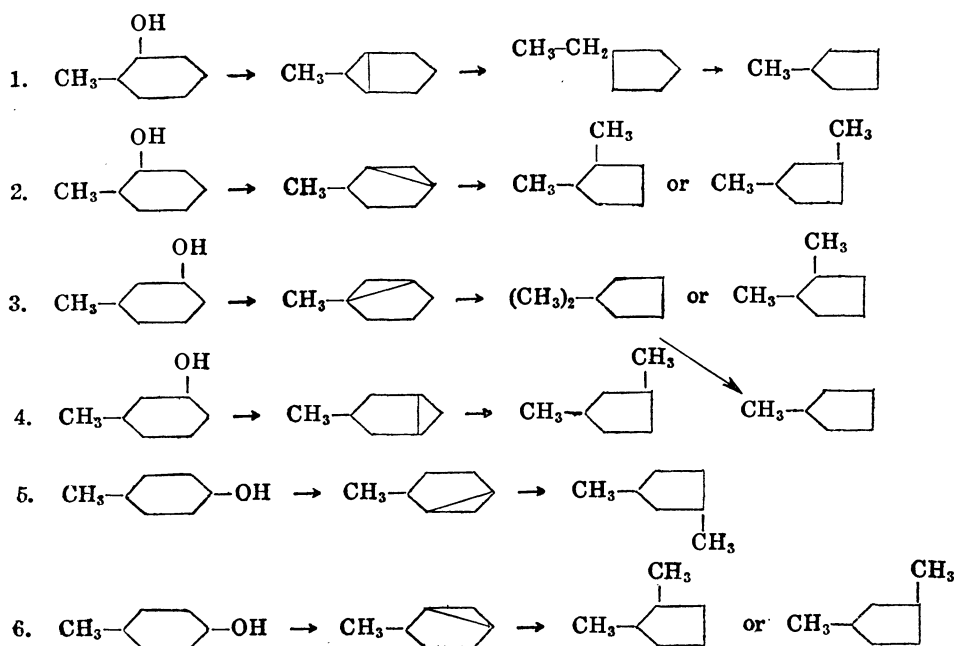
Table 6.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
To 80°	+	0.6887	—	—	—	—	—	—	—
80—85°	0.7	0.7574	0.7403	1.41197	1.40970	1.41766	1.42240	85.80	14.23
85—90°	3.2	0.7764	0.7588	1.41980	1.41743	1.42548	1.43051	85.92	13.95
90—93°	4.4	0.7802	0.7621	1.42190	1.41944	1.42764	1.43259	86.30	13.73
93—95°	4.2	0.7822	0.7656	1.42380	1.42124	1.42951	1.43464	86.33	13.64
95—97°	9.9	0.7866	0.7693	1.42640	1.42385	1.43234	1.43755	86.36	13.62
97—99°	7.9	0.7923	0.7746	1.42970	1.42718	1.43585	1.44106	86.41	13.55
99—102°	14.4	0.7993	0.7824	1.43442	1.43181	1.44080	1.44626	86.66	13.35
102—105°	12.0	0.8071	0.7915	1.44060	1.43777	1.44725	1.45293	87.15	12.92
105—110°	9.4	0.8143	0.7979	1.44496	1.44202	1.45192	1.45805	87.22	12.77
110—115°	1.9	0.8201	0.8036	1.44917	1.44611	1.45640	1.46277	87.48	12.46
115—130°	3.9	—	—	—	—	—	—	—	—
Residue	21.2	—	—	—	—	—	—	—	—
{ A	5.7	0.9198	0.9062	—	—	—	—	—	—
{ B	10.0	0.9338	0.9204	—	—	—	—	—	—
{ C	2.7	0.9761	0.9632	—	—	—	—	—	—

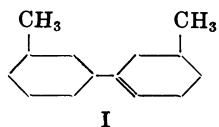
As shown in Table 6, results quite analogous to those in the case of 1-methylcyclohexanol-(3) (cf. Table 4) were obtained.

The above-mentioned experiments show that all the three isomers of methylcyclohexanols undergo the similar isomerisation from the six-membered carbon-rings to the five-membered by the catalytic action of Japanese acid earth heated at 350°, cyclopentane derivatives being produced. As regards the influence of the position of the methyl group in the molecules of methylcyclohexanols on the total yield of cyclopentane derivatives, it is noticed that 1-methylcyclohexanol-(2) is the most easy to be converted into cyclopentane derivatives and 1-methylcyclohexanol-(3) and -(4) follow next, any distinguishable difference being hardly recognized between the latter

two. 1-Methylcyclohexanol-(2) gives, however, the largest yield of cyclopentane and 1-methylcyclohexanol-(4) the smallest, whilst 1-methylcyclohexanol-(3) stands between the two. The mechanism of the formation of cyclopentane derivatives from methylcyclohexanols may be, therefore, explained schematically as follows :



Since ethylcyclopentane and 1,1-dimethylcyclopentane tend to be decomposed to methylcyclopentane and it is difficult for 1,2- and 1,3-dimethylcyclopentanes to produce it, it is very natural that 1-methylcyclohexanol-(2) gives the largest yield of methylcyclopentane and 1-methylcyclohexanol-(4) the smallest as stated above. The yield of methylcyclohexane in the reaction carried out at 250°, on the contrary, is very small in the case of 1-methylcyclohexanol-(2), while in the case of 1-methylcyclohexanol-(3) and -(4), methylcyclohexane is the main reaction product, and the yield of polymers is also in the same order. Markonikoff⁽⁸⁾ obtained the hydrocarbon (I) from Δ^3 -methylcyclohexene by shaking it with 50 per cent. sulphuric acid.



When the above hydrocarbon undergoes the thermal decomposition, it may most probably be decomposed to methylcyclohexane and Δ^3 -methyl-

(8) *Chem. Zentr.*, 1904, I, 1346.

cyclohexene or methylcyclohexadiene and therefore cyclohexene is most easy to occur in the reaction product which is originally rich in Δ^3 -methylcyclohexene as in the case of 1-methylcyclohexanol-(3) or -(4), whereas there is no possibility for 1-methylcyclohexanol-(2) to produce Δ^3 -methylcyclohexene and it is not difficult to anticipate the poor yield of methylcyclohexane in the latter case, which the above experiments have actually shown.

III. Menthol. With regard to the catalytic action of Japanese acid earth on menthol, Ono's paper⁽⁹⁾ was published some years ago. While his experiment was carried out in liquid state, the present author treated menthol in vapour phase with the earth and some interesting facts hitherto unknown were manifested.

By passing 150.0 g. of menthol (m.p., 42° ; $[\alpha]^{18}_D$, $-48^\circ 19'$) on the earth heated at 230° , 94.50 g. of oil (d_4^{20} , 0.8137) and 5.8 g. of water were obtained, and the former gave the fractions shown in Table 7 after subjected to fractional distillation ten times.

Table 7.

B.p.	Yield (g.)	d_4^{20}	d_4^{20}	n_D^{20}	n_a^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
To 80°	0.8	0.6971	0.6805	1.38729	1.38534	1.39753	1.39635	—	—
$80-100^\circ$	1.3	0.7713	0.7563	1.42060	1.41813	1.42636	1.43104	—	—
$100-140^\circ$	1.4	0.7941	0.7789	1.43341	1.43080	1.43962	1.44489	—	—
$140-150^\circ$	1.2	0.8015	0.7860	1.43762	1.43545	1.44337	1.44900	—	—
$150-155^\circ$	0.7	0.8050	0.7913	1.43893	1.43625	1.44487	1.44989	—	—
$155-159^\circ$	2.1	0.8081	0.7941	1.43944	1.43696	1.44537	1.45019	86.34	13.82
$159-162^\circ$	4.9	0.8090	0.7948	1.43994	1.43734	1.44577	1.45058	85.99	14.02
$162-165^\circ$	—	0.8108	0.7974	1.44095	1.43837	1.44656	1.45137	86.00	13.97
$165-168^\circ$	26.9	0.8145	0.8000	1.44285	1.44038	1.44874	1.45362	86.17	13.84
$168-171^\circ$	11.8	0.8203	0.8064	1.44657	1.44400	1.45252	1.45775	86.26	13.68
$171-175^\circ$	4.6	0.8274	0.8140	1.45207	1.44932	1.45850	1.46396	86.49	13.44
$175-180^\circ$	2.8	0.8349	0.8203	1.45906	1.45603	1.46593	1.47186	87.00	13.09
$180-188^\circ$	1.9	0.8488	0.8350	1.46821	1.46509	1.47582	1.48228	87.63	12.58
$188-189^\circ$	1.8	0.8540	0.8411	1.47176	1.46955	1.47958	1.48628	88.24	12.00
Residue	—	—	—	—	—	—	—	—	—
{ A	0.8	0.9129	0.9003	—	—	—	—	—	—
{ B	2.3	0.9470	0.9367	—	—	—	—	—	—

(9) This Bulletin, 1 (1926), 250.

As is seen in Table 7 it is obvious that the main reaction products are menthane and menthene.

When menthol (200.0 g.) was passed on the earth heated at 350°, 19.7 g. of light oil boiling under 100°, 155.0 g. of heavy oil boiling above 100° (d_4^{20} , 0.8061), and 18.2 g. of water were obtained. The oily substances were fractionated ten times and the fractions shown in Table 8 were obtained.

Table 8.

B.p.	Yield (g.)	d_4^{20}	d_4^{20}	n_D^{20}	n_x^{20}	n_p^{20}	n_r^{20}	Analysis (%)	
								C	H
45—50°	1.8	0.6527	0.6342	1.36390	1.36191	1.36819	1.37218	—	—
50—55°	0.5	—	—	1.37855	1.37698	1.38114	—	—	—
55—67°	1.8	0.7035	0.6846	1.38461	1.38263	1.38933	1.39367	84.32	15.76
67—72°	5.7	0.7343	0.7152	1.39780	1.39581	1.40282	1.40733	85.07	15.02
72—75°	1.2	0.7491	0.7310	1.40412	1.40204	1.40914	1.41366	85.30	14.71
75—80°	1.5	0.7561	0.7393	1.40747	1.40541	1.41266	1.41726	85.46	14.68
80—90°	1.7	0.7604	0.7429	1.41044	1.40820	1.41592	1.42029	85.58	14.57
90—100°	1.4	0.7737	0.7561	—	—	—	—	—	—
100—120°	1.9	0.7927	0.7763	1.41960	1.41663	—	1.42980	—	—
120—140°	2.8	0.8106	0.7945	1.43381	1.43070	—	1.44538	87.28	12.85
140—150°	2.8	0.8172	0.8018	1.44546	1.44220	—	1.45824	86.96	13.05
150—153°	1.9	0.8162	0.8007	1.44867	1.44531	—	1.46130	86.75	13.32
153—156°	4.2	0.8155	0.8001	1.44747	1.44420	—	1.45993	86.68	13.39
156—159°	3.0	0.8143	0.7987	1.44657	1.44330	—	1.45844	86.36	13.58
159—162°	12.0	0.8160	0.8003	1.44546	1.44240	—	1.45706	86.52	13.57
162—165°	12.0	0.8176	0.8028	1.44627	1.44320	—	1.45795	86.70	13.44
165—168°	12.2	0.8234	0.8092	1.44747	1.44440	—	1.45933	86.79	13.27
168—171°	8.8	0.8314	0.8174	1.45167	1.44852	—	1.46396	86.90	13.14
171—175°	6.5	0.8402	0.8262	1.45757	1.45423	—	1.47053	87.15	12.90
175—180°	5.7	0.8571	0.8419	1.46464	1.46097	—	1.47864	87.76	12.31
180—185°	5.7	0.8707	0.8550	1.47765	1.47381	—	1.49371	88.34	11.56
185—190°	5.3	0.8832	0.8694	1.48862	1.48426	—	1.50587	88.70	11.25
190—195°	7.1	0.8938	0.8795	1.49805	1.49361	1.50772	—	89.10	10.98
195—200°	1.8	0.8999	0.8859	1.50536	1.50065	1.51559	—	—	—
Residue	4.3	—	—	—	—	—	—	—	—

The fractions boiling near 70° in Table 8 are methylcyclopentane, which was confirmed by the examination of physical constants and results of elementary analyses and further by the oxidation with concentrated

nitric acid, succinic acid (m. p., 177—179°) and acetic acid being thereby found in the oxidation products. Among the fractions boiling between 100° and 200°, those boiling between 160° and 170° predominate in quantity, which seem to be composed of menthene when their densities and refractive indices are considered, but from the fact that they give nitrosochloride or nitrosite with difficulty and also from the calculation of bromine values, the content of menthene was found to be only less than 10 per cent. They probably consist of menthene, menthane, and *p*-cymene. The presence of *p*-cymene was confirmed as follows: the fraction boiling between 171° and 175° was nitrated and the resulting nitro-compound was reduced, aminocymene being then isolated as benzoyl derivative (m. p., 135—136°, probably a mixture of two isomers). The physical constants of the fraction boiling between 140° and 150° well accord with those of isopropylcyclopentane. It is not determined, however, whether that substance is actually present or not. It is remarkable that the fraction boiling between 156° and 159° has a minimum density. This fraction was treated with concentrated sulphuric acid to remove unsaturated hydrocarbons and remaining saturated hydrocarbons were once more fractionated (Table 9).

Table 9.

B.p.	Yield (g.)	d	d_0^{20}	n_D^{20}	n_a^{20}	n_r^{20}	Analysis (%)	
							C	H
152—154°	1.8	0.7941	0.7805	1.43191	1.42940	1.43704	85.89	14.29
154—158°	1.3	0.7980	0.7836	1.43311	1.43070	1.43840	—	—
158—162°	0.9	0.8034	0.7865	1.43462	1.43210	1.43982	—	—

The main portion given in Table 9 is the first fraction boiling between 152° and 154°, which consists most probably of methylisobutylcyclopentane, by the thermal decomposition of which the above-mentioned cyclopentane may be produced. Thus the transformation of menthol by the contact action of Japanese acid earth heated at 350° may be represented by the following scheme :

Table 10. (*Concluded*)

B.p.	Yield (g.)	d_4^{20}	d_4^{30}	n_D^{20}	n_x^{20}	n_D^{20}	n_D^{20}	Analysis (%)	
								C	H
150–154°	3.8	0.8225	0.8069	1.45147	1.44852	1.45839	1.46456	—	—
154–158°	3.0	0.8186	0.8037	1.44887	1.44606	1.45561	1.46140	87.03	13.10
158–161°	7.7	0.8164	0.8021	1.44677	1.44405	1.45322	1.45869	86.67	13.54
161–164°	6.9	0.8174	0.8027	1.44657	1.44390	1.45292	1.45834	—	—
164–167°	10.8	0.8218	0.8069	1.44967	1.44691	1.45620	1.46169	—	—
167–170°	15.0	0.8265	0.8122	1.45317	1.45043	1.45999	1.46570	86.67	13.42
170–173°	10.7	0.8335	0.8238	1.46255	1.45953	1.46939	1.47638	—	—
173–175°	4.5	0.8534	0.8429	1.47755	1.47414	1.48612	1.50139	88.06	11.95
175–180°	6.3	0.8595	0.8544	1.48688	1.48321	1.49631	1.50429	88.62	11.51
180–185°	4.9	0.8851	0.8696	1.49862	1.49454	1.50876	1.51762	—	—
185–190°	5.8	0.8929	0.8784	1.50448	1.50028	1.51503	1.52415	—	—
190–200°	6.0	0.9003	0.8809	1.50924	1.50500	1.52001	1.52927	—	—
Residue	—	—	—	—	—	—	—	—	—

As is seen in Table 10, the presence of menthene, cyclopentane, and methylisobutylcyclopentane is manifested by the physical constants and results of elementary analyses of the fractions with the boiling points corresponding to these substances respectively.

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DIE ZWEIDIMENSIONALE ZUSTANDSGLEICHUNG UND DER BAU VON GRENZFLÄCHENSCHICHTEN.

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Einleitung.

Die adsorbierte Schicht, die sich an der Grenzfläche fest-gasförmig oder flüssig-gasförmig bildet, wird aus jetzt vielfach erkannten Gründen, von denen der Begriff von der lateralen Beweglichkeit der adsorbierten Mole-

küle und ihre experimentelle Bestätigung besonders genannt werden sollen,⁽¹⁾ als eine spezielle zweidimensionale Phase betrachtet. Diese Betrachtung gewährt uns viele Erleichterungen für die Theorie und die Systematik der Adsorptionserscheinungen, indem wir mittels der Zustandsgleichung der adsorbierten Schicht manche empirisch bekannte Beziehungen ableiten können, und dadurch können wir ihre theoretische Deutung gewinnen. Der erste Teil dieser Abhandlung behandelt die Theorie und die Systematik der adsorbierten Schicht, und zwar wird er folgendermassen eingeteilt: 1) Die Zustandsgleichung der adsorbierten Schicht, 2) Adsorptionsgleichungen, 3) Vergleich der theoretischen Beziehungen mit empirischen Daten, 4) Über die Natur der lateralen Zwischenmolekularkräfte, 5) Zur Deutung der Traubeschen Regel.

Die Betrachtungen über die adsorbierte Schicht könnten mit einigen besonderen Berücksichtigungen auch auf die Oberflächenschicht reiner Flüssigkeiten übertragen werden. Stellt man also für die Oberflächenschicht reiner Flüssigkeiten die zweidimensionale Zustandsgleichung auf, so gelangt man zu einer Theorie der Oberflächenspannung überhaupt und zu einer Theorie der Temperaturabhängigkeit der Oberflächenspannung. Der zweite Teil dieser Abhandlung befasst sich mit der Theorie der Oberflächenschicht reiner Flüssigkeiten und zwar wird er eingeteilt wie folgt: 1) Die Zustandsgleichung der Oberflächenschicht reiner Flüssigkeiten, 2) Theorie der Temperaturabhängigkeit der Oberflächenspannung, 3) Über das abnorme Verhalten der anisotropen Flüssigkeiten.

In allen Fällen ist die Rolle der lateralen Zwischenmolekularkräfte in Grenzflächenschichten die Hauptfrage, die in dieser Abhandlung in bezug auf den Bau der Schichten besonders in Betracht gezogen wird. Auch über die Natur der Zwischenmolekularkräfte wird in dieser Abhandlung einiges berichtet.

Teil I. Die adsorbierte Schicht.

1. Die Zustandsgleichung der adsorbierten Schicht.

Die Zustandsgleichung der adsorbierten Schicht wird mittels der Virial-Methode, die von Milne und Fowler für Gase in einer allgemeinen Form angegeben worden ist, folgenderweise hergeleitet⁽²⁾.

Betrachtet man ein Molekül von der Masse m und von der Flächenkoordinaten x, y , das sich unter der Einwirkung einer äusseren Kraft X, Y

(1) Estermann, *Z. Physik*, **33** (1925), 320. Volmer u. Adhikari, *Z. physik. Chem.*, **119** (1926), 46. Cockroft, *Proc. Roy. Soc. London*, A, **119** (1928), 293.

(2) Milne, *Phil. Mag.* (6), **50** (1925), 409; Fowler, „Statistical Mechanics“, Cambridge (1929), S. 211. Vgl. auch Bradley, *Chemical Reviews*, **9** (1931), 47.

und gleichzeitig gegen eine Reibungskraft $-\kappa(\dot{x}, \dot{y})$ bewegt, so hat man für das Molekül folgende Bewegungsgleichung:

$$m\ddot{x} = X - \kappa\dot{x},$$

und noch eine analoge Gleichung. Multipliziert man die Gleichung mit $\frac{1}{2}x$, so ergibt sich:

$$\frac{1}{4} \frac{d^2}{dt^2}(mx^2) + \frac{1}{4} \frac{d}{dt}(\kappa x^2) - \frac{1}{2} m\dot{x}^2 = \frac{1}{2} Xx.$$

Addiert man zwei analoge Beziehungen, so bekommt man:

$$\frac{1}{4} \frac{d^2}{dt^2}(mr^2) + \frac{1}{4} \frac{d}{dt}(\kappa r^2) = \frac{1}{2} mv^2 + \frac{1}{2}(Xx + Yy),$$

wobei gesetzt sind:

$$x^2 + y^2 = r^2 \quad \text{und} \quad \dot{x}^2 + \dot{y}^2 = v^2.$$

Summiert man diese Gleichung über alle Moleküle in der gegebenen Fläche Ω und integriert sie dann über eine lange Zeit τ , so ergibt sich:

$$\frac{1}{\tau} \left[\frac{1}{4} \frac{d}{dt} (\sum mr^2) + \frac{1}{4} \sum \kappa r^2 \right]_0^\tau = \frac{1}{2} \overline{\sum mv^2} + \frac{1}{2} \overline{\sum Xx + Yy},$$

wobei ——— einen Mittelwert von Zeit null bis Zeit τ bedeutet. Wenn das gegebene Materialsystem sich in einem stationären Zustande befindet, so wird der Wert des Ausdruckes [] sowohl für Zeit null als auch für Zeit τ gleich sein und infolgedessen ergibt sich:

$$\frac{1}{2} \overline{\sum mv^2} = -\frac{1}{2} \overline{\sum Xx + Yy}. \quad (1)$$

Dies ist die zweidimensionale Virialgleichung von Clausius.

Für den Fall von der adsorbierten Schicht soll diese Virialgleichung noch folgendermassen erläutert werden. In der Fläche Ω befinden sich insgesamt N Moleküle⁽³⁾, deren thermische Bewegung auf die Grenzlinie der Schicht einen Flächendruck Π (Dyn/cm.) bewirken. Das Virial besteht in diesem Fall aus den Druckkräften, die die Grenzlinie hindurch wirken, und den Zwischenmolekularkräften. Bezeichnet man mit dl ein Linienelement

(3) Mit N bezeichnen wir unten die Loschmidtsche Zahl.

und mit p, q die Richtungscosinus von der Senkrechten auf das Linienelement, so werden die Druckkomponente $-p\Pi dl$, $-q\Pi dl$, die sich an dem Virial :

$$\frac{1}{2} \Pi \int (px + qy) dl$$

beteiligen. Dies wird nach dem Greenschen Theorem gleich :

$$\frac{1}{2} \Pi \iint \left(\frac{dx}{dx} + \frac{dy}{dy} \right) d\Omega = \Pi \Omega . \quad (2)$$

Man nimmt nun zwischen den Molekülen eine Kraft von der Form $-\frac{\partial E}{\partial r}$ an. Betrachtet man zwei benachbarte Moleküle von den Flächenkoordinaten (x, y) und (x', y') , die sich unter der Einwirkung der Zwischenmolekularkräfte befinden, deren Kraftkomponente (X, Y) und (X', Y') sind, so ergeben sich :

$$X = -\frac{\partial E}{\partial r} \frac{x-x'}{r}, \quad X' = -\frac{\partial E}{\partial r} \frac{x'-x}{r}.$$

Daraus folgt :

$$xX + x'X' = -\frac{\partial E}{\partial r} \frac{(x-x')^2}{r}.$$

Die Molekularkräfte zwischen dem in Betracht kommenden Molekülpaare beteiligen sich demnach an dem Virial :

$$\frac{1}{2} r \frac{\partial E}{\partial r}.$$

Dies wird, indem man es über alle Paare der Moleküle summiert :

$$\frac{1}{2} \sum r \frac{\partial E}{\partial r}. \quad (3)$$

Kombiniert man die Beziehungen (2) und (3) mit (1), so erhält man :

$$\Pi \Omega = \frac{1}{2} \sum mv^2 - \frac{1}{2} \sum r \frac{\partial E}{\partial r}, \quad (4)$$

was eine allgemeine zweidimensionale Zustandsgleichung darstellt.

Verwendet man hierfür den Energie-Gleichverteilungssatz :

$$\frac{1}{2} \sum mv^2 = NkT,$$

wobei k die Boltzmannsche Konstante und T die absolute Temperatur ist, und gibt der mittleren Zahl der Paare der Moleküle, deren Kraftzentren zwischen r und $r+dr$ sind :

$$\frac{1}{2} N^2 e^{-\frac{E}{kT}} \frac{2\pi r \cdot dr}{\Omega},$$

so wird die Gleichung (4) folgendermassen ausgedrückt :

$$P\Omega = NkT - \frac{1}{4} \frac{N^2}{\Omega} 2\pi \int_0^\infty r^2 \frac{\partial E}{\partial r} e^{-\frac{E}{kT}} dr. \quad (5)$$

Durch Integration folgt :

$$P\Omega = NkT - \frac{N^2 \pi kT}{\Omega} \int_0^\infty r (e^{-\frac{E}{kT}} - 1) dr, \quad (6)$$

wobei angenommen ist :

$$\lim_{r \rightarrow \infty} r^2 (e^{-\frac{E}{kT}} - 1) = 0.$$

Setzt man in die letzte Gleichung

$$N\pi \int_0^\infty r (1 - e^{-\frac{E}{kT}}) dr = B \quad (7)$$

ein, so wird :

$$P\Omega = NkT + \frac{NkTB}{\Omega}, \quad (8)$$

wo B den zweiten Virialkoeffizient bedeutet. Dies wird noch einfacher ausgedrückt :

$$P(\Omega - B) = NkT, \quad (9)$$

denn annähernd gesetzt wird :

$$P = \frac{NkT}{\Omega}.$$

Nimmt man an, dass sich die Moleküle wie harte Kugeln verhalten und dass sie nur bis zu einem bestimmten Grenzabstand (r_0) aneinander herankommen können, so wird der zweite Virialkoeffizient ausgedrückt :

$$B = B_0 + N\pi \int_{r_0}^{\infty} r(1 - e^{-\frac{E}{kT}}) dr, \quad (10)$$

wobei B_0 den Grenzwert des Flächenbedarfs (pro N Moleküle) bedeutet. Setzt man hierfür weiter ein :

$$A = N^2 \pi kT \int_{r_0}^{\infty} r(e^{-\frac{E}{kT}} - 1) dr, \quad (11)$$

so wird Gleichung (9) :

$$\left(\Pi + \frac{A}{\Omega^2}\right)(\Omega - B_0) = NkT, \quad (12)$$

was die zweidimensionale van der Waalssche Gleichung darstellt.

Zweckmässiger schreibt man diese Gleichung in der Form :

$$\Pi(\Omega - B_0) = iNkT, \quad (13)$$

wobei gesetzt ist :

$$i = 1 - \frac{A}{NkT\Omega} = 1 - \frac{N\pi}{\Omega} \int_{r_0}^{\infty} r(e^{-\frac{E}{kT}} - 1) dr, \quad (14)$$

oder in der Form :

$$\Pi\Omega = jNkT, \quad (15)$$

wobei gesetzt ist :

$$j = 1 - \frac{A}{NkT\Omega} + \frac{B_0}{\Omega}. \quad (16)$$

Die Gleichungen (9), (13), (15) sind diejenigen, die ich im folgenden mannigfaltig verwenden möchte.

2. Adsorptionsgleichungen.

Wenn man einmal für die adsorbierte Schicht die Zustandsgleichung aufstellt, so werden die bekannten Adsorptionsgleichungen von Langmuir, Schmidt, Freundlich und damit zusammenhängende Beziehungen hergeleitet, indem man dabei die Gibbssche Gleichung mitberücksichtigt; derartige Herleitung habe ich schon in meinen vorhergehenden Arbeiten angegeben⁽⁴⁾. Hier soll eher eine anderweitige thermodynamische Herleitung, die von Hückel⁽⁵⁾ vertreten worden ist, wiedergegeben werden und zwar in bezug

(4) Tamamushi, Dieses Bulletin, **1** (1926), 185 ; 257 ; **8** (1933), 120.

(5) Hückel, „ Adsorption und Kapillarkondensation, “ Leipzig (1928), S. 188.

auf die Langmuirsche und Freundlichsche Isotherme, damit man ihre theoretischen Zusammenhänge einsehen kann.

Man stellt nun zwischen Gas- oder Lösungsphase und adsorbierte Phase ein thermodynamisches Gleichgewicht vor. Das ganze Materialsystem wird charakterisiert durch :

$$\Phi(n, V, \Omega, T) = 0 ,$$

wo n die Anzahl der insgesamt vorhandenen Molen, V das Volum des Gas- oder Lösungsraumes, Ω die Fläche der adsorbierten Phase und T die absolute Temperatur bedeutet. Nun wird n folgendermassen ausgedrückt, indem man mit c die Konzentration in der Gas- oder Lösungsphase und mit a die Konzentration in der adsorbierten Phase bezeichnet :

$$n = Vc + \Omega a .$$

Bezeichnet man mit F die freie Energie des ganzen Systems, mit U die gesamte Energie und mit S die Entropie, so wird F folgenderweise gegeben :

$$F = U - TS = F' + Vf + \Omega \mathfrak{f} ,$$

wo $F' = U' - TS'$ die freie Energie des von Adsorptiv freien Adsorbens, $f = u - Ts$ die freie Energie (pro cm^3) im innern des Gases oder der Lösung und $\mathfrak{f} = u - T\mathfrak{s}$ den Überschuss an freier Energie (pro cm^2) der Oberfläche bedeutet. Man hat hierbei f als Funktion von c , T , und $\mathfrak{f}$ als Funktion von a , T anzusehen. Bildet man die Variation von der freien Energie bei konstanten V , Ω , T und setzt diese gleich null, so erhält man die thermodynamische Gleichgewichtsbedingung :

$$\delta F = V \left(\frac{\partial f}{\partial c} \right)_T \delta c + \Omega \left(\frac{\partial \mathfrak{f}}{\partial a} \right)_T \delta a = 0 .$$

Berücksichtigt man, dass

$$n = Vc + \Omega a$$

konstant ist, und somit dass

$$V\delta c + \Omega\delta a = 0$$

ist, so wird die Bedingung :

$$\left(\frac{\partial f}{\partial c} \right)_T = \left(\frac{\partial \mathfrak{f}}{\partial a} \right)_T . \quad (17)$$

Für ein ideales Gas oder eine ideale Lösung hat die freie Energie f (pro cm^3) folgende Form :

$$f = cC_v(T - T \log T) + RTc \log c + c(\bar{u}_0 - \bar{s}_0 T),$$

wobei C_v die Molarwärme bei konstantem Volum, $\bar{u}_0$ ein konstanter Energiewert (pro Mol) und $\bar{s}_0$ ein konstanter Entropiewert (pro Mol) bedeutet. Daraus folgt :

$$\left(\frac{\partial f}{\partial c}\right)_T = C_v(T - T \log T) + RT(1 + \log c) + \bar{u}_0 - \bar{s}_0 T.$$

Für den Fall, wo man für die adsorbierte Phase eine ideale zweidimensionale Gas-Gleichung d. h. $\Pi Q = RT$ aufstellen kann, wird die freie Energie des adsorbierten Stoffes (pro cm^2) ganz analog derjenigen bei der dreidimensionalen Phase gegeben in der Form :

$$f = aC_v'(T - T \log T) + RTa \log a + a(\bar{u}_0 - \bar{s}_0 T),$$

wo C_v' die Molarwärme des adsorbierten Stoffes, $\bar{u}_0$ ein konstanter Energiewert (pro Mol) und $\bar{s}_0$ ein konstanter Entropiewert (pro Mol) ist. Daraus folgt :

$$\left(\frac{\partial f}{\partial a}\right)_T = C_v'(T - T \log T) + RT(1 + \log a) + \bar{u}_0 - \bar{s}_0 T.$$

Die Molarwärme des Stoffes in der adsorbierten Phase C_v' wird aber hierbei gleich derjenigen im Gas- oder Lösungsraum C_v angesehen werden, sofern der Stoff in den beiden Phasen sich ideal verhält⁽⁶⁾. Bei Gleichgewicht hat man also :

$$RT \log c + \bar{u}_0 - \bar{s}_0 T = RT \log a + \bar{u}_0 - \bar{s}_0 T,$$

oder

$$\log a = \log c + \frac{\bar{u}_0 - \bar{u}_0}{RT} + \frac{\bar{s}_0 - \bar{s}_0}{R}.$$

Man setzt hierzu die Energiegleichungen :

$$\bar{u} = C_v T + \bar{u}_0, \quad \bar{u} = \bar{u} - \varphi = C_v T + \bar{u}_0 - \varphi,$$

wo $\bar{u}$ die gesamte Energie (pro Mol) der Gas- oder Lösungsphase, $\bar{u}$ diejenige der adsorbierten Phase bedeutet. Hieraus folgt :

$$\bar{u}_0 - \bar{u}_0 = \bar{u} - \bar{u} = \varphi,$$

(6) Vgl. Einstein, *Ann. Physik*, (4), 4 (1901), 513.

wo φ das Adsorptionspotential darstellt. Man setzt weiter :

$$\frac{\bar{s}_0 - \bar{s}_0}{R} = \log \Delta ,$$

wo Δ eine Grösse von der Dimension [L] ist⁽⁷⁾, die aber nur statistisch berechnet werden könnte.

Man hat demnach schliesslich :

$$a = \Delta c e^{\frac{\varphi}{RT}} . \quad (18)$$

Dies ist die Adsorptionsgleichung, die von Williams, Henry, Eucken, Jaquet und Hückel molekularkinetisch abgeleitet worden ist⁽⁸⁾.

Für den Fall von grössern adsorbierten Mengen, stellt man für die adsorbierte Schicht die Gleichung (9) :

$$\Pi(\Omega - B) = RT ,$$

oder

$$\Pi = \frac{RT}{\Omega - B} = \frac{RT}{\Omega} \left(1 + \frac{B}{\Omega} + \dots \right) \quad (19)$$

auf. Die freie Energie $\bar{f}$ (pro Mol) des adsorbierten Stoffes lässt sich aus Π folgenderweise berechnen :

$$\bar{f} = - \int \Pi d\Omega + f_0(T) ,$$

wo $f_0(T)$ eine Funktion der Temperatur ist. Dies wird nach (19) :

$$\bar{f} = -RT \left(\log \Omega - \frac{B}{\Omega} - \dots \right) + f_0(T) ,$$

oder

$$\bar{f} = RT (\log a + Ba + \dots) + f_0(T) ,$$

(7) Nach van Laar (*Z. Physik*, **45** (1927), 635.) wird die Entropiekonstante $\bar{s}_0$ von Gasen gleich $-R \log v_0$ gesetzt werden, wo v_0 das sogenannte Elementarvolum [L³] ist. Wenn die Entropiekonstante der adsorbierten Phase ebenfalls gleich $-R \log \omega_0$, wo ω_0 die Elementaroberfläche [L²] bedeutet, gesetzt werden könnte, so würde :

$$\frac{\bar{s}_0 - \bar{s}_0}{R} = \log \frac{v_0}{\omega_0} = \log \Delta ,$$

wo Δ eine Grösse von der Dimension [L] ist.

(8) Williams, *Proc. Roy. Soc. London*, A, **96** (1920), 287 ; 298. Henry, *Phil. Mag.*, (6), **44** (1922), 689. Eucken, *Z. Elektrochem.*, **28** (1922), 6. Jaquet, *Fortschritte d. Chem., Physik u. physik. Chem.*, **18** (1925), Nr. 7. Hückel, loc. cit.

da $a = \frac{1}{Q}$ ist. Die freie Energie $\bar{f}$ (pro cm^2) lässt sich ausdrücken :

$$\bar{f} = a\bar{f},$$

woraus folgt :

$$\begin{aligned} \left(\frac{\partial \bar{f}}{\partial a}\right)_T &= \bar{f} + a\left(\frac{\partial \bar{f}}{\partial a}\right)_T = RT(\log a + Ba + \dots) + f_0(T) \\ &+ aRT\left(\frac{1}{a} + B + \dots\right) = RT(1 + \log a + 2Ba + \dots) + f_0(T). \end{aligned}$$

Nimmt man die Gas- oder Lösungsphase, die sich mit der adsorbierten Phase im Gleichgewicht befindet, auch in diesem Fall als ideal an, so hat man für die freie Energie (pro cm^3) :

$$f = cC_v(T - T \log T) + RTc \log c + c(\bar{u}_0 - \bar{s}_0 T),$$

und demnach folgt :

$$\left(\frac{\partial f}{\partial c}\right)_T = C_v(T - T \log T) + RT(1 + \log c) + \bar{u}_0 - \bar{s}_0 T.$$

Die Gleichgewichtsbedingung wird also :

$$\begin{aligned} C_v(T - T \log T) + RT(1 + \log c) + \bar{u}_0 - \bar{s}_0 T \\ = RT(1 + \log a + 2Ba + \dots) + f_0(T), \end{aligned}$$

oder

$$\log a + 2Ba + \dots = \log c + \frac{f(T)}{RT},$$

wobei zur Abkürzung gesetzt ist :

$$f(T) = C_v(T - T \log T) + \bar{u}_0 - \bar{s}_0 T - f_0(T).$$

Hieraus folgt :

$$a = c e^{\frac{f(T)}{RT} - 2Ba - \dots}. \quad (20)$$

Diese Gleichung stimmt mit der Langmuirschen Isotherme :

$$c = \frac{\eta a}{1 - N\xi a}$$

überein, wo η und ξ Konstanten sind, indem gesetzt sind :

$$e^{\frac{f(T)}{RT}} = \frac{1}{\eta},$$

und

$$e^{-2Ba \cdots} = 1 - 2Ba = 1 - N\xi a.$$

In dieser Beziehung bleibt aber $f(T)$ bzw. η noch unbestimmt, was nur statistisch berechnet werden könnte⁽⁹⁾.

Wenn man schliesslich für die adsorbierte Schicht die Zustandsgleichung (15):

$$H\Omega = jRT$$

aufstellt, so kommt man jetzt zur Freundlichschen Isotherme. Ganz analog wie oben gezeigt ist, verhält es sich mit der Gleichgewichtsbedingung:

$$C_v(T - T \log T) + RT(1 + \log c) + \bar{u}_0 - \bar{s}_0 T = jRT(1 + \log a) + f'_0(T),$$

wo $f'_0(T)$ eine Funktion von der Temperatur ist. Dies wird:

$$\log a = \frac{1}{j}(\log c + 1 - j) + \frac{f'(T)}{RT},$$

wobei gesetzt ist:

$$f'(T) = C_v(T - T \log T) + \bar{u}_0 - \bar{s}_0 T - f'_0(T).$$

Es folgt also hieraus:

$$a = c^{\frac{1}{j}} e^{\frac{f'(T)}{RT} + \frac{1}{j} - 1}. \quad (21)$$

Diese Beziehung stimmt mit der bekannten Formel:

$$a = \alpha c^{\frac{1}{n}}, \quad (22)$$

überein, indem gesetzt sind:

$$e^{\frac{f'(T)}{RT} + \frac{1}{j} - 1} = \alpha \quad \text{und} \quad n = j.$$

Die erste Konstante α könnte auch nur statistisch berechnet werden. Über die Deutung der zweiten Konstante n bzw. j soll in folgender Abschnitt einiges bemerkt werden⁽¹⁰⁾.

(9) Die statistische Ableitung der Langmuirschen Isotherme wurde von Kar (*Physik. Z.*, **26** (1925), 615.) und von Th. Sxsl (*Z. Physik*, **48** (1928), 607.) angegeben.

(10) Siehe auch Tamamushi, Dieses Bulletin, **8** (1933), 120.

3. Vergleich der theoretischen Beziehungen mit empirischen Daten.

Wenn die adsorbierte Schicht soweit verdünnt ist, dass dabei kein Virial mehr berücksichtigt zu werden braucht, so wird die Zustandsgleichung in die Form :

$$\Pi\Omega = NkT \quad (23)$$

gefasst. Eine derartige Schicht, die dieser Gleichung folgt und die eine ideale Gasschicht genannt wird, ist aber nur selten zu realisieren. Es ist Adam und Jessop gelungen mittels der Langmuirschen Wage direkt zu beweisen, dass diese Gleichung bei den verdünnten Schichten von den Estern der zweibasischen Säuren ($\text{C}_2\text{H}_5\text{OOC}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$, $n = 10, 11$) annähernd gilt, und sie konnten zeigen dass die Gaskonstante k für die zweidimensionale Phase mit derjenigen der dreidimensionalen Phase, innerhalb der möglichen Messungsgenauigkeit, übereinstimmt⁽¹¹⁾. Indirekt könnte man aber diese Gleichung folgenderweise prüfen. Für den Oberflächendruck wird :

$$\Pi = \sigma_M - \sigma_L$$

eingesetzt, wobei σ_M die Oberflächenspannung des reinen Lösungsmittels, und σ_L diejenige der Lösung bedeutet. Weiter ist Ω gleich $\frac{1}{a}$, und so folgt aus Gleichung (23) :

$$\sigma_M - \sigma_L = NkTa . \quad (24)$$

Die adsorbierte Menge a ist nun anderweitig mittels der Gibbsschen Gleichung angegeben, nämlich :

$$a = - \frac{c}{RT} \frac{d\sigma}{dc} . \quad (25)$$

Aus Gleichung (24) und (25) ergibt sich :

$$\sigma_M - \sigma_L = Kc ,$$

wo K eine Konstante ist. Diese Beziehung wurde schon in früher Zeit von Traube⁽¹²⁾ erkannt, und neulich auch von mir⁽¹³⁾ bei den Lösungen von zweibasischen Säuren als gültig gefunden. In solchen Fällen ist die

(11) Adam u. Jessop, *Proc. Roy. Soc., A*, **112** (1926), 376. Neuere Versuche von Guastalla (*Compt. rend.*, **189** (1929), 241.) ergaben auch den richtigen k -Wert.

(12) Traube, *Ann.*, **265** (1891), 27.

(13) Tamamushi, *Dieses Bulletin*, **7** (1932), 168.

thermische Bewegung der adsorbierten Moleküle die einzige Ursache des Sinkens der Oberflächenspannung.

Die Zustandsgleichung :

$$\Pi(\Omega - \beta) = RT \quad (26)$$

ist zuerst von Volmer⁽¹⁴⁾ gleichsam versuchsweise aufgestellt worden. Diese unterscheidet sich aber von der oben angestellten Gleichung (9), indem β nicht den Virial-Koeffizient, sondern einfach die Korrektur für den Flächenbedarf der adsorbierten Moleküle bedeutet. Volmer hat gezeigt, dass die Gültigkeit dieser Gleichung entweder direkt (wie bei Benzophenon an Quecksilberoberfläche) oder indirekt d. h. durch Vergleichung der thermodynamischen Folgerung mit den bisherigen Erfahrungstatsachen bewiesen werden kann. Im letzten Fall leitet man die Langmuirsche Isotherme aus Gleichung (26) und der Gibbsschen Gleichung her, und dann berechnet man aus der Beziehung zwischen der Langmuirschen Isotherme und der Szyszkowskischen empirischen Formel⁽¹⁵⁾ den Wert von $\frac{2\beta}{N}$, der eigentlich kinetisch die vierfache wirkliche Flächenbedeckung eines Moleküls darstellt, wie in der folgenden Tabelle gezeigt ist.

Tabelle 1.

Stoff	$\frac{2\beta}{N}$	Beobachter
Essigsäure	45×10^{-16} qcm.	Traube
Propionsäure	42 „	„
Buttersäure	31 „	Szyszkowski
Valeriansäure	31 „	„
Capronsäure	31 „	„
Heptylsäure	22 „	Forch
Octylsäure	16 „	„

Dass der berechnete Wert von $\frac{2\beta}{N}$ beim Ansteigen in der homologen Reihe nicht konstant ausfällt, sondern deutlich kleiner wird, hat einen zu der Annahme geführt, dass an der Oberfläche die Orientierung von Molekülen nicht gleichmässig stattgefunden hätte. Es scheint aber hieraus

(14) Volmer, *Z. physik. Chem.*, **115** (1925), 239 ; 253.

(15) Szyszkowski, *Z. physik. Chem.*, **64** (1908), 385.

über die Orientierung von Molekülen noch keinen eindeutigen Schluss gezogen werden zu können. (Vgl. Abschnitt 5.)

Sollte man nicht hier nicht nur die Flächenkorrektur, sondern auch die Wechselwirkung der adsorbierten Moleküle in Betracht ziehen? Dann müsste man eher für die Daten von Szyszkowski und ändern die Zustandsgleichung (9):

$$\Pi(\Omega - B) = RT,$$

wo B den zweiten Virialkoeffizient bedeutet, oder die mit dieser Gleichung gleichwertige Gleichung (13):

$$\Pi(\Omega - B_0) = iRT$$

anwenden. Diese letzte Gleichung ist zuerst von Rideal und Schofield⁽¹⁶⁾ in bezug auf die Versuche von Szyszkowski, Frumkin und andern und später von mir⁽¹⁷⁾ in bezug auf die Versuche von Traube und Schmidt geprüft worden. Die folgende Tabelle zeigt die Ergebnisse für die homologen normalen Fettsäuren.

Man sieht also, dass der Grenzwert vom Flächenbedarf $\frac{B_0}{N}$ eines Mole-

Tabelle 2.

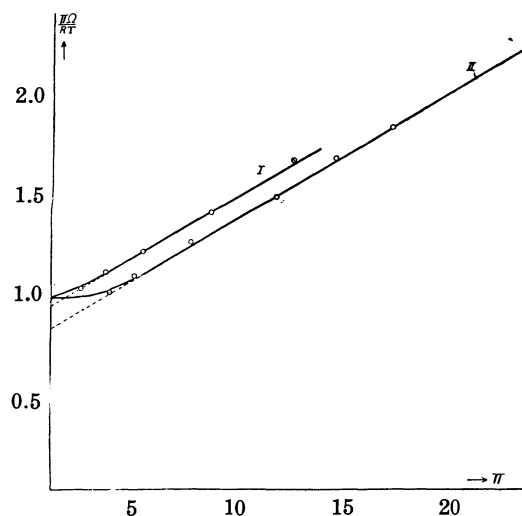
Stoff	$\frac{B_0}{N}$	i	Beobachter
Essigsäure	24.3×10^{-16} qcm.	0.97	Traube
Propionsäure	24.3 „	0.85	„
Buttersäure	24.3 „	0.73	Szyszkowski
Valeriansäure	24.3 „	0.63	„
Capronsäure	24.3 „	0.43	„
Caprylsäure	24.3 „	0.46	„
Caprinsäure	24.3 „	0.35	Frumkin
Laurinsäure	24.3 „	0.23	„

küls an der Grenzfläche Wasser-Luft bei der homologen Reihe strikt konstant ausfällt, während sich der Koeffizient i mit der Molekulargrösse beinahe regelmässig vermindert. Die Grösse 24.3×10^{-16} qcm. für den Flächenbedarf stimmt sowohl mit der Grösse eines Kettenkopfes der langgestalteten Moleküle, die von Langmuir sowie von Adam bei den unlöslichen

(16) Rideal u. Schofield, *Proc. Roy. Soc., A*, **109** (1925), 58.

(17) Tamamushi, *Dieses Bulletin*, **2** (1927), 299.

Schichten ermittelt wurde, als auch mit dem röntgenographisch bestimmten Querschnitt des Moleküls überein⁽¹⁸⁾. Dies hat sicherlich den Grund darin, dass auch die Moleküle der löslichen Fettsäuren an der Oberfläche des Wassers dicht aneinander stabartig gegen die Oberfläche stehen, und zwar tritt diese Orientierung schon bei nicht hohen Konzentrationen ein, was man aus dem Verlaufe der $\frac{\Pi Q}{RT}$, Π -Kurve vermuten könnte. Der Wert von dem Koeffizient i ergibt sich durch die Extrapolation des geradlinigen Teils der $\frac{\Pi Q}{RT}$, Π -Kurve (Fig. 1). Der Wert von $1-i$ ausfällt hierbei immer positiv, dies bedingt, wie man aus Gleichung (14) sieht, zwischen den adsorbierten Molekülen die Anziehungskräfte, auf deren Natur in Abschnitt 4 näher eingegangen wird.



I: Essigsäure, II: Propionsäure

Fig. 1.

Aus Gleichung (9) und der Gibbsschen Gleichung ergibt sich folgende Beziehung:

$$\frac{B}{RT} \Pi + \log \Pi = \log c + k,$$

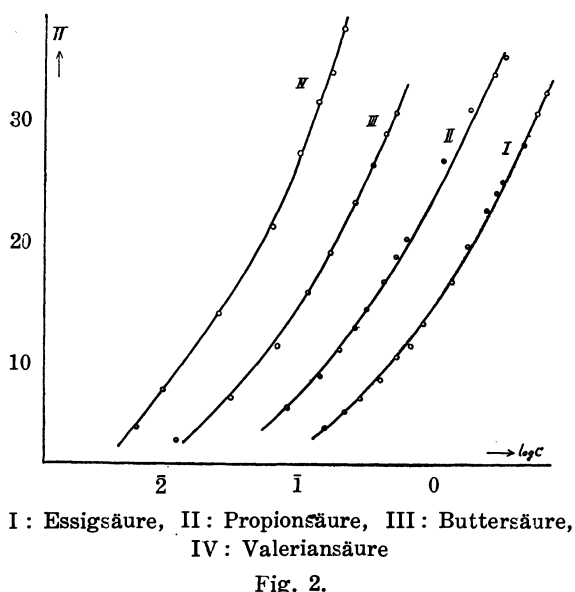
wo k eine Integrationskonstante ist. Diese Beziehung ist in der Form der Szyszkowskischen Formel analog und gibt ebenso zufriedenstellend die empirischen Daten wieder. Für den Fall der sehr hohen Konzentrationen, wo $\log \Pi$ gegen Π übersehen werden kann, ergibt sich:

$$\frac{B}{RT} \Pi = \log c + k,$$

was einen lineären Zusammenhang zwischen Π und $\log c$ darstellt. Ein derartiger Sachverhalt wird tatsächlich aus Fig. 2 erkannt werden⁽¹⁹⁾.

(18) Siehe „Handbuch d. Physik“, Bd. 24, zweiter Teil (1933), S. 32.

(19) Fig. 2 sowie Fig. 3 und 4 sind nach meinen demnächst veröffentlichten Versuchen über einen grösseren Bereich der Konzentration gezeichnet.



Wenn man für die adsorbierte Schicht die Zustandsgleichung (15):

$$\Pi \Omega = jRT$$

verwendet, so ergibt sich aus dieser und der Gibbsschen Gleichung:

$$j \log \Pi = \log c + k,$$

oder

$$\Pi = kc^{\frac{1}{j}}, \quad (27)$$

was analog der Freundlich'schen Adsorptionsisotherme eine exponente Beziehung zwischen Π und c ausdrückt.

Im Vergleich der Gleichung (15) mit der zweidimensionalen van der Waalsschen Gleichung (12), lässt sich j folgendermassen schreiben (16):

$$j = 1 - \frac{A}{RT\Omega} + \frac{B_0}{\Omega}.$$

Der Wert von j kann also entweder grösser oder kleiner als 1 sein, je nachdem:

$$-\frac{A}{RT\Omega} + \frac{B_0}{\Omega} > 0 \quad \text{oder} \quad -\frac{A}{RT\Omega} + \frac{B_0}{\Omega} < 0$$

ist. Dementsprechend wird die Π , c -Kurve entweder konkav oder konvex nach c -Achse verlaufen. Wenn ich meine Daten von den niedrigen Fettsäuren in Π , c -Ebene niederschreibe, so erhalte ich mehr oder weniger nach c -Achse konkav verlaufende Kurven. (Fig. 3.)

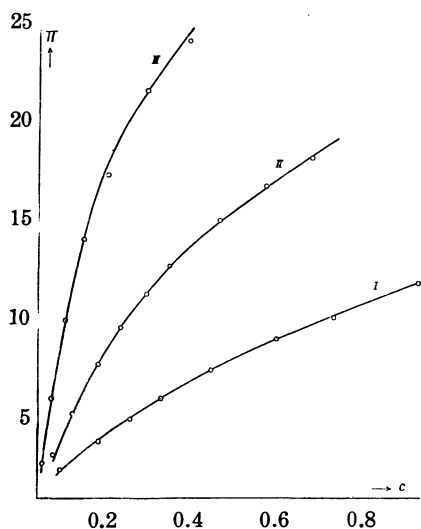
Dies deutet darauf hin, dass dabei j immernoch grösser als 1 ausfällt und demnach gilt:

$$-\frac{A}{RT} + B_0 > 0.$$

Dies kann so sein, wenn entweder $A < 0$ (Abstossung) ist, oder $A > 0$ (Anziehung) ist. Der letzte Fall ist aber gültig unter der Bedingung:

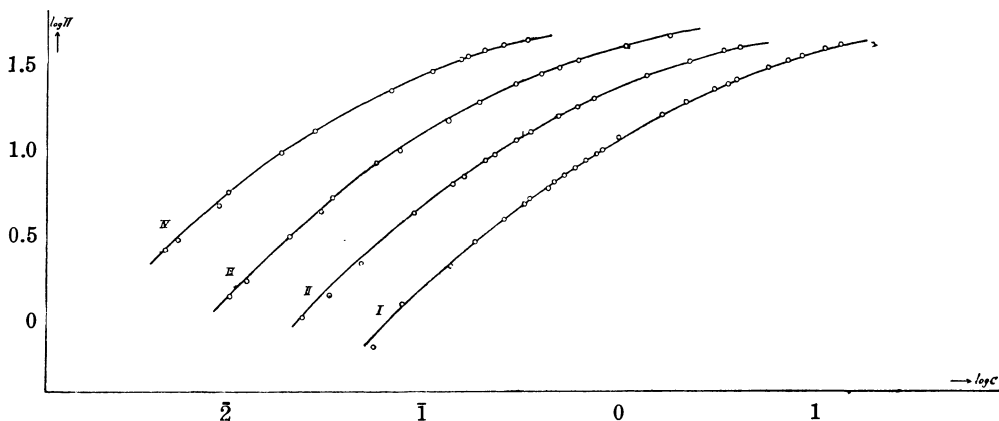
$B_0 > \frac{A}{RT}$ d. h. wenn die Korrektur des Flächenbedarfs diejenige der Kohäsion übertrifft⁽²⁰⁾.

Fig. 4 zeigt die $\log \Pi$, $\log c$ -Kurven für die niedrigen Fettsäuren. Man sieht hier, dass die Kurven anfänglich bei sehr kleinen Konzentrationen annähernd linear und zwar mit der Neigung von 45 Grad gegen die $\log c$ -Achse, dann werden sie nach schwachem Umbiegen wieder fast linear im mittleren Konzentrationsbereich, und dann bei grösseren Konzentrationen verlaufen sie allmählich konkav gegen die $\log c$ -Achse. Dementsprechend ändert sich der Wert von j , nämlich, er wird annähernd gleich 1 im Anfang, etwas grösser in dem mittleren Teil und dann nimmt er desto mehr zu, je höher die Konzentration wird; aller-



I: Essigsäure, II: Propionsäure,
III: Buttersäure

Fig. 3.



I: Essigsäure, II: Propionsäure, III: Buttersäure, IV: Valeriansäure

Fig. 4.

(20) In meiner früheren Arbeit über den Einfluss der Gase auf die Oberflächenspannung von Flüssigkeiten habe ich auch die Beziehung (27) erkannt, wo j gleich etwa 3 war. Es handelte sich dabei um Adsorption von Luft, N_2O , CO_2 , und H_2S an Wasser-, C_2H_5OH -, C_6H_6 -Oberfläche und es kämen möglicherweise zwischen den adsorbierten Molekülen abstossende Kräfte zur Wirkung, also $A < 0$, damit j grösser als 1 sein könnte. Dieses Bulletin, 1 (1926), 173.

dings vollzieht sich die Veränderung über das ganze Gebiet nur allmählich und die Kurve verläuft im ganzen schwach konkav nach $\log c$ -Achse. Eine solche Veränderung charakterisiert ja den Koeffizient j sowohl in Beziehung (27) als auch in der Freundlich'schen Adsorptionsisotherme, und deren Deutung scheint für den Mechanismus der Adsorption besonders wichtig zu sein. Über die theoretische Deutung der Freundlich'schen Isotherme habe ich schon in meiner vorhergehenden Arbeit einiges berichtet⁽²¹⁾. Es gibt noch darüber eine ausführliche experimentelle Arbeit von Wöhler und Wenzel⁽²²⁾, in der man das charakteristische Verhalten der Konstanten α und n in der Isotherme (22) überschauen kann.

4. Über die Natur der lateralen Zwischenmolekularkräfte.

In der zweidimensionalen van der Waalsschen Gleichung (12) :

$$\left(H + \frac{A}{\Omega^2} \right) (\Omega - B_0) = RT$$

kann A im allgemeinen positiv oder negativ sein d. h. die lateralen Zwischenmolekularkräfte wirken anziehend oder abstossend, während im Fall der Gase sie stets anziehend ausfallen. Dass A hierbei tatsächlich positiv oder negativ sein kann, hängt von dem elektrischen Bau der adsorbierten Moleküle und ihrer Orientierung an der Grenzfläche ab. Denkt man z. B. Dipolmoleküle, deren elektrischer Dipol asymmetrisch im Molekül liegt, so kann man in der Tat eine derartige Orientierung annehmen, dass sie abstossende Kräfte zwischen Molekülen bedingt. Derartige Abstossungskräfte sind von Magnus⁽²³⁾ für adsorbierte Kohlensäure an Kohle mit Erfolg angenommen worden.

Stellt man die Gleichung (12) in der Form (13) :

$$H(\Omega - B_0) = iRT$$

auf, so wird der Koeffizient i kleiner oder grösser als 1, je nachdem zwischen Molekülen ein Anziehungs- oder Abstossungspotential zur Wirkung kommt. Für den Fall von der adsorbierten Essigsäure an Kohle, ergibt sich i grösser als 1⁽²⁴⁾. Dagegen ergibt sich i für den Fall von den adsorbierten Fettsäuren an der Oberfläche des Wassers immer kleiner als 1 und zwar vermindert er sich fast regelmässig mit der Molekulargrösse (Tabelle 2). Der Ausdruck

(21) Tamamushi, Dieses Bulletin, **8** (1933), 120.

(22) Wöhler u. Wenzel, *Kolloid-Z.*, **53** (1930), 273.

(23) Magnus, *Z. anorg. allgem. Chem.*, **158** (1926), 67.

(24) Tamamushi, Dieses Bulletin, **2** (1927), 299.

$RT(1-i)$ stellt dabei das Anziehungspotential dar, das sich dementsprechend mit der Molekulargrösse vermehrt. Über diesen Sachverhalt soll unten etwas näher diskutiert werden.

Man betrachtet hier die langgestalteten Moleküle der Fettsäuren, die ein festes Dipol an der polaren Endgruppe besitzen. Das Kraftpotential zwischen den Molekülen lässt sich als Summe dreier Potentialfunktionen schreiben:

$$E = \pm \epsilon_s - \epsilon_D + b(r) .$$

Hier stellt ϵ_s die klassische elektrostatische Wechselwirkung zwischen den Dipolen dar, diese besteht eigentlich aus zwei Effekten d. h. Orientierungs- und Induktionseffekt. Diese Wechselwirkung könnte anziehend oder abstossend sein, je nachdem die gegenseitige Orientierung der Dipole an der Oberfläche es erfordert, sie ist also mit zwei Vorzeichen versehen worden. Dagegen ist ϵ_D das Potential der Dispersionskräfte d. h. die quantenmechanische Störung zweiter Ordnung der kurzperiodischen Elektronenbewegung innerhalb der Moleküle⁽²⁵⁾. Die Wechselwirkung zwischen den nonpolaren Ketten wäre meistens in ihrer Natur der letzte genannte Effekt, der immerhin anziehend wirkt. Schliesslich stellt $b(r)$ die Funktion einer intensiven Abstossung dar, die aber mit dem Abstand plötzlich verschwindet, von deren Effekt man hier absehen könnte. Nun bedingt die parallele Orientierung von Molekülen der Fettsäuren, die weitgehend an der Oberfläche des Wassers demonstriert wurde, zwischen den Ketten immer ein Anziehungspotential, soweit die Ketten ziemlich dicht aneinander gelegt sind. In welchem Sinne aber das Potential zwischen den polaren Köpfen bei gleicher Orientierung von Molekülen wirkt, ist noch fraglich, denn man hat keine genauen Kenntnisse über die gegenseitige Orientierung der Dipolvektoren in Molekülen. Mir scheint es doch angebracht, hier auch zwischen den polaren Köpfen ein Anziehungspotential anzunehmen. Der Grund dafür ist, dass das gesamte Potential für die niedrigsten Glieder der Fettsäuren, bei denen die Wechselwirkung zwischen den Ketten im Vergleich derjenigen zwischen den Köpfen als klein angesehen werden könnte, noch anziehend ausfällt, sofern die adsorbierten Schichten der Gleichung (13) folgen, wobei der Koeffizient i sich kleiner als 1 zeigt.

Ein Anziehungspotential wird ja zwischen den Köpfen z. B. durch eine solche gegenseitige Orientierung der Dipolachsen zur Wirkung kommen, wie Fig. 5 zeigt; jeder Dipol hat also vier Nachbarn und die Dipolachsen sind zueinander mit 45 Grad geneigt, indem zwischen den Dipolen ein Anziehungspotential resultiert. Das Potential zwischen zweien Dipolen wird dann:

(25) London, *Z. Physik*, **63** (1930), 245.

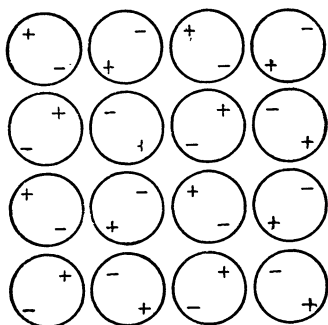


Fig. 5.

$$\epsilon = \frac{3}{2} \frac{\mu^2}{r^3},$$

wo μ das Dipolmoment und r den Abstand der Dipolzentren bedeutet.

Ich nehme weiter an, dass nur ein statischer Orientierungseffekt zum Virial beiträgt. Im allgemeinen wird diese Annahme nicht berechtigt werden, aber dies wäre für die niedersten Glieder der Fettsäuren in grober Annäherung gestattet, wo die Dispersionskräfte zwischen den Ketten gegen die statischen Kräfte zwischen den Köpfen übersehen werden könnten. Man könnte demnach folgende Abschätzung durchführen. Die Wechselwirkungsenergie (pro Mol) lässt sich nach (14) schreiben :

$$\begin{aligned} RT(1-i) &= \frac{A}{\Omega} = \frac{N^2 \pi k T}{\Omega} \int_{r_0}^{\infty} r (e^{-\frac{E}{kT}} - 1) dr \\ &= \frac{N^2 \pi}{2\Omega} \int_{r_0}^{\infty} r^2 \frac{\partial E}{\partial r} e^{-\frac{E}{kT}} dr. \end{aligned}$$

Setzt man hier

$$E = \frac{3}{2} \frac{\mu^2}{r^3}$$

ein, so folgt :

$$\begin{aligned} RT(1-i) &= -\frac{N^2 \pi}{2\Omega} \int_{r_0}^{\infty} r^2 \frac{9}{2} \frac{\mu^2}{r^4} dr \\ &= -\frac{9}{4} \frac{N^2 \pi \mu^2}{\Omega} \int_{r_0}^{\infty} \frac{dr}{r^2} = \frac{9}{4} \frac{N^2 \pi \mu^2}{\Omega r_0}. \end{aligned}$$

Man nimmt hierbei an :

$$\Omega = N r_0^3,$$

so ergibt sich :

$$RT(1-i) = \frac{9}{4} \frac{N \pi \mu^2}{r_0^3},$$

oder

$$kT(1-i) = \frac{9}{4} \frac{\pi \mu^2}{r_0^3}.$$

Aus den bekannten Werten von $kT(1-i)$ lässt sich nun μ berechnen, indem man für r_0 einen wahrscheinlichen Wert (5 Å) einsetzt. In Tabelle 3 sind die berechneten Dipolmomente ($\mu_{ber.}$) gezeigt, daneben sind einmal die dielektrisch gemessenen Dipolmomente ($\mu_{diel.}$) und ein anderesmal die aus Daten der Grenzflächenpotential ermittelten Dipolmomente ($\mu_{pot.}$) angegeben.

Die berechneten Momente sind also im Mittelwert etwas zu klein im Vergleich mit den dielektrisch gemessenen, sie sind dagegen etwas zu gross im Vergleich mit aus der Grenzflächenpotential ermittelten. Die Ergebnisse sind aber schliesslich mehr oder weniger zufällig, denn die

Tabelle 3.

Stoff	$\mu_{ber.}$	$\mu_{diel.}^{(26)}$	$\mu_{pot.}^{(28)}$
Essigsäure	0.15×10^{-18}	0.75×10^{-18}	—
Propionsäure	0.33 „	0.63 „	—
Buttersäure	0.49 „	0.66 „	0.306×10^{-18}
i-Valeriansäure	0.57 „	—	0.309 „
Capronsäure	0.71 „	—	0.305 „

gegenseitige Neigung der Dipolachsen bzw. der Zahlenfaktor der Potentialfunktion wurde oben etwas willkürlich angenommen und auch der Induktionseffekt wurde dabei nicht berücksichtigt. Durch die gegenseitige polarisierende Wirkung, die nicht nur zwischen Fettsäure-Dipolen sondern auch zwischen Fettsäure-Dipol und Wasser-Dipol hervortreten soll, wird das eigene Dipolmoment der Fettsäure weitgehend verändert. Ob ist die Ermittlungsmethode des Dipolmomentes mittels den Daten der Grenzflächenpotentiale sachlich noch nicht einwandfrei⁽²⁷⁾, so bleibt auch die Ermittlung mittels den Daten der Kohäsion nur in grober Annäherung. Immerhin dürften die beiden Methoden in beuzg auf den Mechanismus der Molekularorientierung als fruchtbar angesehen werden⁽²⁸⁾.

(26) Dipolmoment berechnet als Einfachmolekül. Briegleb, *Z. physik. Chem.*, B, **10** (1930), 205. Neuere Messungen ergaben grössere Momenten: Zahn, *Phys. Rev.*, **37** (1931), 1516; Wilson u. Wenzke, *J. Chem. Physics*, **2** (1934), 546.

(27) Williams u. Vigfusson, *J. Phys. Chem.*, **35** (1931), 345.

(28) Vgl. Rideal, „Surface Chemistry“, 2. Aufl. (1930), S. 340.

Die Notwendigkeit, die Dispersionskräfte in Betracht zu ziehen, tritt deutlich hervor, sobald wir bei den höheren Glieder der homologen Säuren ankommen. Die fast regelmässige Steigerung der Kohäsion mit der Molekulargrösse (Tabelle 2) lässt sich nicht verstehen durch den rein elektrostatischen Effekt, der sehr wahrscheinlich für jedes Glied der Säuren beinahe gleich gross bleiben müsste, sondern lässt sich nur verstehen durch den quantenmechanischen Effekt, der sich in seinem Charakter additiv verhält. Nach London⁽²⁹⁾ wird die Wechselwirkungsenergie zweier unangeregter elementar gebauter Moleküle folgendermassen ausgedrückt :

$$\varepsilon_D = -\frac{3}{4} \frac{h\nu_0\alpha^2}{r^6},$$

wo r den festen Abstand zweier Moleküle, h die Plancksche Konstante, ν_0 die Eigenfrequenz der isolierten Dipole und α die Polarisierbarkeit darstellt. Die Anwendung dieser Attraktionsformel auf die kompliziert gebauten Moleküle wie Kohlenstoffketten könnte aber nur einiger Begrenzung gestattet werden. Die Bedingung $r^3 \gg \alpha$ ist aber hierbei fast ausreichend erfüllt, indem eingesetzt sind: $r = 5 \times 10^{-8}$ und $\alpha = 10 \sim 20^{-24}$. Die Notwendigkeit, auf die unterschiedliche Attraktionsfähigkeit der einzelnen Molekülbezirke Rücksicht zu nehmen, ist hier keineswegs zu ignorieren. Aber in roher Abschätzung dürfte doch diese Formel hierfür verwendet werden.

Nun könnte r für jedes Glied der homologen Fettsäuren als gleich gross angenommen werden, ν_0 würde dagegen mit der Kettenlänge abnehmen. Da aber α^2 gleichzeitig schneller zunehmen wird, so würde die Wechselwirkungsenergie im Ganzen mit der Kettenlänge anwachsen. Demnach wäre die Polarisierbarkeit α für den Anwachs der Kohäsionsenergie verantwortlich. Die Polarisierbarkeit berechnet sich nun aus optischen Daten mittels der bekannten Beziehung :

$$\frac{4}{3} \pi \alpha N = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \cdot \frac{M}{\rho} (= R_\infty).$$

Die folgende Tabelle gibt R_D (Molarrefraktion für die D-Linie), R_∞ (Molarrefraktion für unendlich lange Wellen) von den normalen homologen Fettsäuren an.

(29) London, *Z. physik. Chem.*, B, **11** (1930), 222.

Tabelle 4⁽³⁰⁾.

Stoff	Mess. Temp.	R_D	R_∞
Essigsäure	20	12.99	12.8
Propionsäure	20	17.51	17.3
Buttersäure	20	22.16	22.0
Valeriansäure	22	26.82*	26.5*
Capronsäure	20	31.38	31.0
Heptylsäure	20	36.05	35.7
Caprylsäure	21	40.71	40.2
Nonylsäure	22	45.29*	44.9*
Caprinsäure	42	50.05*	49.7*
Undecylsäure	40	54.75*	54.0*
Laurinsäure	55	59.45*	58.8*

In Tabelle 5 ist α im Vergleich der lateralen Kohäsion $RT(1-i)$ (pro Mol) angegeben. Dort sind auch der Siedepunkt (T_s) und die Verdampfungswärme (λ), die mit der Kohäsion in engem Zusammenhang stehen, angezeigt.

Tabelle 5.

Stoff	α	$RT(1-i)$	T_s	λ (bei T_s , kcal.) ⁽³¹⁾
Essigsäure	25.4	17.4	118	5.83
Propionsäure	46.5	86.9	141	9.55
Buttersäure	75.2	156	162	10.04
Valeriansäure	108	214	185	10.31
Capronsäure	149	331	205	11.5
Caprylsäure	250	313	237	—
Caprinsäure	384	377	269	—
Laurinsäure	538	446	225 (100 mm.)	—

Man sieht, dass α mit der Molekulargrösse ziemlich rasch und regelmässig anwächst; auch wachsen $RT(1-i)$, T_s und λ , nicht ebenso rasch aber beinahe additiv mit der Molekulargrösse an. Nicht vollkommene

(30) Die Daten mit * sind aus meinen unveröffentlichten Versuchen; die andere sind aus den Landolt-Börnsteinschen Tabellen.

(31) Briegleb, *Z. physik. Chem.*, B, **10** (1930), 205.

Additivität in der Kohäsion und in den damit zusammenhängenden Eigenschaften kommt wahrscheinlich aus dem Umstande, dass die Attraktionsfähigkeit der einzelnen Molekülbezirke verschieden ist. Der Grund des Anwachsens der lateralen Kohäsion mit der Molekulargrösse wird aber im wesentlichen mit Recht im quantenmechanischen Effekt gesucht werden.

Die Existenz der lateralen Zwischenmolekularkräfte scheint bei der Strukturbildung der Adsorptionsschicht eine wichtige Rolle zu spielen. Wenn auch die Schicht nicht so weit verdichtet ist, dass die nonpolaren Ketten dicht aneinander zusammengedrängt sind, so würden sich doch die polaren Köpfe elektrostatisch gegenseitig beeinflussen. Sobald die Schicht genügend verdichtet ist, so kommt das Anziehungspotential zwischen den Ketten zur Wirkung und dadurch entsteht eine dicht zusammengepackte monomolekular orientierte Schicht. Da die Anziehungskräfte zwischen den Ketten mit der Kettenlänge zunehmen, so ist die leichtere Strukturbildung bei den länger gestalteten Molekülen verständlich.

Nach der Adamschen Auffassung⁽³²⁾ über den flüssigausgedehnten Schichten der unlöslichen Fettsäuren ziehen die polaren Köpfe einander an, während sich die Ketten durch die thermische Bewegung auseinanderzutrennen versuchen. Diese Auffassung nähert sich der oben angegebenen Auffassung über adsorbierte Schichten der löslichen Fettsäuren, in der Hinsicht, dass die beiden Auffassungen zwischen den polaren Köpfen ein Anziehungspotential annehmen. In welcher Weise dann das Anziehungspotential zwischen den Köpfen zur Wirkung kommt, darüber denkt Lowry⁽³³⁾, dass die Carboxyl-Gruppen durch die Koordination von H-Atomen aneinander gekettet seien, während ich dabei für das Anziehungspotential geeignete gegenseitige Orientierung von Dipolachsen annehmen möchte. Wenn die Adamsche Auffassung berechtigt wäre, so würde also diese Auffassung dadurch verständlich werden, dass man zwischen den Molekülen zwei Anziehungskräfte, nämlich, 1) die elektrostatischen Kräfte zwischen den polaren Köpfen, und 2, die Dispersionskräfte zwischen den Kohlenwasserstoffketten annimmt, wo die ersten Kräfte, die sich mit dem Abstand wie $1/r^4$ vermindert, länger ausbleibt gegen die thermische Bewegung, als die zweiten, die sich mit dem Abstand wie $1/r^7$ vermindert.

In welchem Grössenverhältnis die beiden Wechselwirkungsenergien bei den Molekülen von einer gegebenen Säure und deren Orientierung stehen, diese Frage wird im allgemeinen nicht leicht beantwortet, denn die

(32) Adam, „The Physics and Chemistry of Surfaces“, 1930, S. 75; *Nature*, **126** (1930), 955.

(33) Lowry, *Nature*, **127** (1931), 165.

beiden Energien können ohne Willkür nicht jedes für sich abgeschätzt werden. Es scheint aber angebracht anzunehmen, dass bei gleicher Orientierung die statische Energie für jedes Glied der homologen Säuren beinahe konstant bleibt, während die Dispersionsenergie mit der Kettenlänge anwächst.

Die Grössengrenze der gesamten Kohäsionsenergie könnte noch folgenderweise ermittelt werden. Die adsorbierten Schichten der löslichen Fettsäuren folgen der Beziehung (27) :

$$\Pi = kc^{\frac{1}{j}},$$

wo

$$j = 1 - \frac{A}{RT\Omega} + \frac{B_0}{\Omega}$$

ist, und zwar j grösser als 1 ausfällt. Dies bedingt :

$$B_0 > \frac{A}{RT} \quad \text{oder} \quad A < B_0 NkT,$$

soweit A positiv (Anziehungspotential) ist. Setzt man hier für B_0 den Flächenbedarf pro Mol d. h. $6.06 \times 10^{23} \times 24.3 \times 10^{-16}$ und für NkT $6.06 \times 10^{23} \times 4 \times 10^{-14}$ ein, so wird die Bedingung :

$$A < 36 \times 10^{13} \text{ c. g. s. (pro Mol).}$$

Berechnet man nochmals die statische Wechselwirkungsenergie zwischen den Dipolen pro Mol mittels der Beziehung :

$$A = \frac{9}{4} \frac{N^2 \pi \mu^2}{r_0},$$

indem man $r_0 = 5 \times 10^{-8}$ und $\mu = 0.3 \times 10^{-18}$ (ermittelt aus Grenzflächenpotential) ein, so ergibt sich : $A = 5 \times 10^{13}$ c. g. s. Also macht die statische Energie etwa 1/7 der maximalen gesamten Energie aus. Dank diesem Umstand dürften die oben angegebenen Betrachtungen im wesentlichen als berechtigt angesehen werden.

5. Zur Deutung der Traubeschen Regel.

Die Szyszkowskische Formel, die die Abhängigkeit der Oberflächenspannung (σ) von der Konzentration (c) der kapillaraktiven Lösung wiedergibt, lässt sich folgendermassen ausdrücken :

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = b \log \left(\frac{c}{a} + 1 \right), \quad (28)$$

wo b und a Konstanten sind, und zwar ist b von Stoff zu Stoff meist wenig verschieden, während a die für die Kapillaraktivität des Stoffes charakteristische Grösse ist. Man bildet die reziproke Konstante $\frac{1}{a} = \mathfrak{D}$ und nennt dies die spezifische Kapillaraktivität, und mit Hilfe dieser Konstante kann man die Traubesche Regel zahlenmässig fassen. Bildet man den Quotienten $\frac{\mathfrak{D}_{n+1}}{\mathfrak{D}_n}$ für je zwei aufeinanderfolgende Stoffe einer homologen Reihe, so ist dieser so gut wie konstant und hat einen Wert von ungefähr 3. Die Traubesche Regel lässt sich dann folgenderweise formulieren:

$$\frac{\mathfrak{D}_{n+1}}{\mathfrak{D}_n} = e^{\mathfrak{k}(M_{n+1} - M_n)}, \quad (29)$$

wo $\mathfrak{k}$ eine Konstante und M das Molargewicht ist, und zwei in der homologen Reihe aufeinanderfolgende Stoffe sind mit den Reihenzahlen n und $n+1$ charakterisiert. Nun gilt für sehr kleine adsorbierte Menge die Adsorptionsgleichung (18):

$$\frac{a}{c} = A e^{\frac{\varphi}{RT}}.$$

Weiter ist $\frac{a}{c}$ dem $\mathfrak{D}$ proportional, denn bei kleinen Konzentrationen folgt aus der Szyszkowskischen Formel und der Gibbsschen Gleichung folgende Beziehung:

$$\frac{a}{c} = \frac{b\sigma_M}{RT} \cdot \frac{1}{a} = \frac{b\sigma_M}{RT} \mathfrak{D}, \quad (30)$$

wo $\frac{b\sigma_M}{RT}$ als eine Konstante betrachtet wird. Dies in Gleichung (18) eingesetzt und die konstanten Grössen zu einer neuen Konstante A' vereinigt, ergibt:

$$\mathfrak{D} = A' e^{\frac{\varphi}{RT}},$$

und für je zwei aufeinanderfolgende Stoffe einer homologen Reihe:

$$\frac{\mathfrak{D}_{n+1}}{\mathfrak{D}_n} = e^{\frac{1}{RT}(\varphi_{n+1} - \varphi_n)}. \quad (31)$$

Aus Gleichung (29) und (31) folgt :

$$\varphi_{n+1} - \varphi_n = RTf(M_{n+1} - M_n) . \quad (32)$$

Die Traubesche Regel besagt also : zwischen je zwei aufeinanderfolgenden Stoffen einer homologen Reihe besteht ein konstanter Unterschied in den Arbeiten, die erforderlich sind, um ein Mol des Stoffes aus der Oberfläche in die Lösung zu bringen, und zwar wächst diese Arbeit um den konstanten Betrag mit dem Wachsen des Molargewichtes.

Langmuir⁽³⁴⁾ zog hieraus den Schluss, dass die Ketten der Moleküle flach an der Oberfläche lägen, indem jede neu hinzukommende CH₂-Gruppe den gleichen Betrag an Arbeit wie jede vorangehende beiträgt. Dieser Schluss von Langmuir ist aber neuerdings von Cassel und Formstecher⁽³⁵⁾ bezweifelt worden. Sie meinen, dass die Moleküle der löslichen Fettsäuren auch in den verdünnten Oberflächen senkrecht zur Oberfläche stehen, und sie deuten die Traubesche Regel, die trotzdem giltig ist, in der Weise dass sie schliessen, dass die Kohlenwasserstoffkette durch die Kohäsionskräfte des Wassers aus dem Innern um so kräftiger herausgedrängt wird, je länger sie ist. Welcher Schluss bei der Betrachtung der verdünnten Oberfläche der Fettsäure-Lösungen zutrifft, scheint aber noch nicht entschieden werden können.

Auch in den Fällen von den adsorbierten Oberflächen zweibasischer Fettsäuren, die von mir⁽³⁶⁾ untersucht wurden, ist die Traubesche Regel giltig. Dabei ist die flache Lagerung der Kohlenwasserstoffkette höchst wahrscheinlich, da das Molekül an den beiden polaren Endgruppen gleichmässig ins Wasser gezogen wird. Dagegen mag das Molekül einbasischer Säuren auch in verdünnter Oberfläche nicht wagerecht liegen, sondern senkrecht stehen, indem eine hydrophile Gruppe stark ins Wasser hineingezogen wird. Immerhin müsste die Casselsche Deutung über den Mechanismus des Adsorptionsvorganges noch analysiert werden.

Ich werde aber hier nicht auf den Adsorptionsvorgang bei den verdünnten Schichten der einbasischen Säuren eingehen, sondern ich möchte den Fall von ziemlich verdichteten Adsorptionsschichten, wo eine senkrechte Stellung der Moleküle von keiner Seite beweifelt wird, betrachten und möchte zeigen, wie auch dabei die Traubesche Regel giltig bleiben kann.

Die Szyszkowskische Formel selbst gibt die empirische Daten über einen grossen Bereich der Konzentrationen gut wieder. Die gleichen Daten werden aber ebenso vorzüglich von der Gleichung (9) :

(34) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1886.

(35) Cassel u. Formstecher, *Kolloid-Z.*, **61** (1932), 18. Vgl. auch Freundlich, *Ergebnisse d. exakt. Naturwissenschaften*, **12** (1933), 101.

(36) Tamamushi, loc. cit. (13).

$$\Pi(\Omega - B) = RT,$$

oder (13) :

$$\Pi(\Omega - B_0) = iRT$$

wiedergegeben, was ich schon im Abschnitt 3 besprochen habe. In Tabelle 1 und 2 sieht man die Werte von β bzw. B und i . Sowohl B als auch i nehmen mit der Molekulargrösse ab, was darauf hindeutet, dass sich die Kohäsionskräfte mit der Molekulargrösse vermehren. Auf jeden Fall ist die Verwendbarkeit dieser Gleichungen (9), (13) für die ziemlich verdichteten Schichten ein Beweis der Existenz der Kohäsionskräfte in diesen Schichten.

Nun wird die spezifische Kapillaraktivität auch hierbei durch $\mathfrak{D}$ bezeichnet. Die Beziehung (30), die besagt, dass $\frac{a}{c}$ dem $\mathfrak{D}$ proportional ist, könnte auch hier bei verdichteten Schichten ohne weiteres verwendet werden, denn sie bedingt nur, dass die Bulkonzentration c klein ist und nicht, dass die adsorbierte Menge a klein ist. Stellt man für die adsorbierte Schicht die Zustandsgleichung :

$$\Pi(\Omega - B) = RT$$

auf, so bekommt man die Adsorptionsgleichung (20) :

$$\frac{a}{c} = e^{\frac{f(T)}{RT} - 2 \frac{B}{\Omega} - \dots\dots}$$

Die gesamte Adsorptionsenergie besteht also jetzt aus zwei Teilen: 1) $-\frac{2B}{\Omega}RT$

eine Arbeit, die erforderlich ist, um dicht zusammengepackte Moleküle voneinander zu lösen, 2) $f(T)$ eine Arbeit, die erforderlich ist, um die jetzt durch die erste Arbeit von einander gelösten Moleküle von der Oberfläche zum Innern der Lösung zu bringen. Aus Gleichung (20), (30), und (31) folgt :

$$\frac{\mathfrak{D}_{n+1}}{\mathfrak{D}_n} = \frac{1}{e^{RT}} \{ f(T)_{n+1} - f(T)_n \} - 2 \left\{ \left(\frac{B}{\Omega} \right)_{n+1} - \left(\frac{B}{\Omega} \right)_n \right\},$$

oder

$$\frac{\mathfrak{D}_{n+1}}{\mathfrak{D}_n} = e^{\frac{1}{RT}} \{ f(T)_{n+1} - f(T)_n \} + \frac{2}{RT} \left\{ \left(\frac{A}{\Omega} \right)_{n+1} - \left(\frac{A}{\Omega} \right)_n \right\},$$

unter Berücksichtigung von Gleichungen (10), (11) :

$$B = B_0 + N\pi \int_{r_0}^{\infty} r \left(1 - e^{-\frac{E}{kT}} \right) dr,$$

$$\begin{aligned}\frac{B}{Q} &= \frac{B_0}{Q} + \frac{N\pi}{Q} \int_{r_0}^{\infty} r(1 - e^{-\frac{E}{kT}}) dr, \\ -\left(\frac{B}{Q}\right)_{n+1} + \left(\frac{B}{Q}\right)_n &= \left\{ \frac{N\pi}{Q} \int_{r_0}^{\infty} r(e^{-\frac{E}{kT}} - 1) dr \right\}_{n+1} - \left\{ \frac{N\pi}{Q} \int_{r_0}^{\infty} r(e^{-\frac{E}{kT}} - 1) dr \right\}_n \\ &= \frac{1}{RT} \left\{ \left(\frac{A}{Q}\right)_{n+1} - \left(\frac{A}{Q}\right)_n \right\}.\end{aligned}$$

Setzt man hierfür der Einfachheit halber :

$$f(T)_{n+1} - f(T)_n = f_{n+1} - f_n,$$

und

$$2\left(\frac{A}{Q}\right)_{n+1} - 2\left(\frac{A}{Q}\right)_n = \psi_{n+1} - \psi_n$$

ein, so ergibt sich :

$$\frac{\mathfrak{D}_{n+1}}{\mathfrak{D}_n} = e^{\frac{1}{RT}(f_{n+1} - f_n) + \frac{1}{RT}(\psi_{n+1} - \psi_n)} \quad (33)$$

Wenn die rechte Seite dieser Beziehung konstant wäre, so würde die Traubesche Regel gelten. Nun ist die Energiedifferenz $f_{n+1} - f_n$ nicht mehr an sich konstant, wie es bei verdünnten Schichten war, und so wäre der Mechanismus des Vorganges verschieden von dem bei verdünnten Schichten, wenn auch die Traubesche Regel hier noch gilt. Die Bedingung, dass :

$$f_{n+1} - f_n + \psi_{n+1} - \psi_n = \text{constans}$$

ist, wäre aber gleichsam durch den folgenden Mechanismus erfüllt, nämlich, dass die Inkonzanz der Differenz der einfachen Adsorptionsenergie $f_{n+1} - f_n$ durch die Inkonzanz der Differenz der Kohäsionsenergie $\psi_{n+1} - \psi_n$ gerade kompensiert werde. Diese Aufstellung wird noch folgenderweise analysiert. Wir betrachten hier die zur Oberfläche senkrecht und aneinander parallel stehenden Moleküle. Wir nehmen an, dass das Potential f_n für jede CH_2 -Gruppe nicht gleichwertig ist, sondern dass es sich um einen konstanten Betrag vermindert beim Sinken der Gruppe von der Oberfläche. Setzt man also für die erste CH_2 -Gruppe das Potential f , für die zweite $f - \delta f$ usw. an, so wird das Gesamtpotential eines n CH_2 -Gruppe haltigen Moleküls :

$$f_n = f + (f - \delta f) + \dots + \{f - (n-1)\delta f\},$$

und das Potential eines $n+1$ CH₂-Gruppe haltigen Moleküls :

$$f_{n+1} = f + (f - \delta f) + \dots + \{f - (n-1)\delta f\} + (f - n\delta f).$$

Somit ergibt sich :

$$f_{n+1} - f_n = f - n\delta f. \quad (34)$$

Die Energiedifferenz zwischen je zwei aufeinander folgenden Molekülen ist also nicht konstant, sondern abhängig vom Wert der Zahl n und zwar nimmt sie mit der Vermehrung der Zahl n ab.

Wir kommen nun bei der Energiedifferenz $\psi_{n+1} - \psi_n$ an. Man nimmt dabei an, dass sich das Kohäsionspotential für jede CH₂-Gruppe bei der Verlängerung der Kette um einen konstanten Betrag vermehrt. Bezeichnet man mit ψ das Potential der ersten CH₂-Gruppe, mit $\psi + \delta\psi$ der zweiten usw., so wird das Gesamtpotential eines n CH₂-Gruppe haltigen Moleküls :

$$\psi_n = \psi + (\psi + \delta\psi) + \dots + \{\psi + (n-1)\delta\psi\},$$

und das Potential eines $n+1$ CH₂-Gruppe haltigen Moleküls :

$$\psi_{n+1} = \psi + (\psi + \delta\psi) + \dots + \{\psi + (n-1)\delta\psi\} + (\psi + n\delta\psi).$$

Dabei ist angenommen, dass jede CH₂-Gruppe einzeln den eigenen Anteil zum Gesamtpotential beiträgt. Daraus folgt :

$$\psi_{n+1} - \psi_n = \psi + n\delta\psi. \quad (35)$$

Dies sagt, dass die Arbeit, die nötig ist, um jede CH₂-Gruppe eines Moleküls gegen die Kohäsion von dem benachbarten Molekül frei zu machen verschieden ist, je nachdem die Gruppe seicht oder tief in der Kettenlänge liegt, und dass die Energiedifferenz zwischen je zwei aufeinanderfolgenden CH₂-Gruppen nicht konstant ist, sondern wächst mit dem sich vergrößernden n an.

Wenn die Bedingungen (34) und (35) erfüllt wären, so würde folgen :

$$f_{n+1} - f_n + \psi_{n+1} - \psi_n = f + \psi - n(\delta f - \delta\psi).$$

Angenommen ist hier noch :

$$\delta f \doteq \delta\psi,$$

so wird :

$$f_{n+1} - f_n + \psi_{n+1} - \psi_n = f + \psi = \text{constans} .$$

Dies in Gleichung (33) eingesetzt, und wir gelangen :

$$\frac{\mathfrak{D}_{n+1}}{\mathfrak{D}_n} = \text{constans} ,$$

was die Traubesche Regel wiedergibt.

(Fortsetzung folgt.)

THE FORMATION OF CYCLIC COMPOUNDS FROM DERIVATIVES OF DIPHENYL. PART III. OPTICAL RESOLUTION OF 6-NITRO-6'-ACETAMIDODIPHENIC ACID, AND FORMATION OF 5-NITROPHENANTHRIDONE-4-CARBOXYLIC ACID THEREFROM.

By Shin-ichi SAKO.

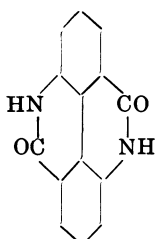
Received July 19th, 1934. Published September 28th, 1934.

In Parts I⁽¹⁾ and II⁽²⁾ of this series, an account was given of the experiments showing that, whilst formation of five- or six-membered rings through the 2- and 2'-positions of optically active diphenyl compounds leads always to inactive products, no such disappearance of activity takes place when seven- or eight-membered rings are formed by linking the 2- and 2'-positions. The importance attached to these observations from the point of view of structure of the substances concerned is that they afford very convincing evidence for the coplanar structure of compounds containing five- or six-membered rings on the one hand, and for the non-coplanar structure of such substituted diphenyls and in substances containing seven- or eight-membered rings on the other. It will be noticed that, in the experi-

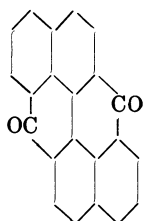
(1) Sako, *Mem. Coll. Eng., Kyushu Imp. Univ.*, **6** (1932), 263.

(2) Sako, this Bulletin, **9** (1934), 55.

ments referred to above, it is only in the formation of six-membered rings, namely, in that of compounds (I)⁽³⁾ and (II)⁽⁴⁾ from 6,6'-diacetamidodiphenic acid and 2,2'-dicarboxy-1,1'-dinaphthyl respectively, that two rings, one on either side of the diphenyl molecule, are formed, a result which is natural for diphenyl-compounds having such structures as the two just mentioned.



(I)

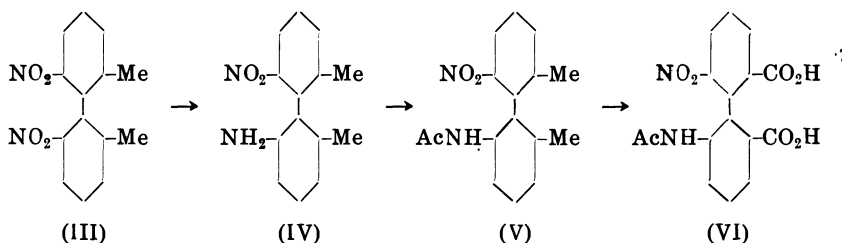


(II)

The present investigation was instituted with the object of obtaining information regarding a compound which, as in those possessing five-, seven-, or eight-

membered rings, has only one six-membered ring formed through the 2- and 2'-positions of 2,2',6,6'-substituted diphenyl.

As the compound capable of producing only one six-membered ring, 6-nitro-6'-acetamidodiphenic acid was chosen, which was prepared from 2,2'-dimethyl-6,6'-dinitrodiphenyl by the following series of processes :



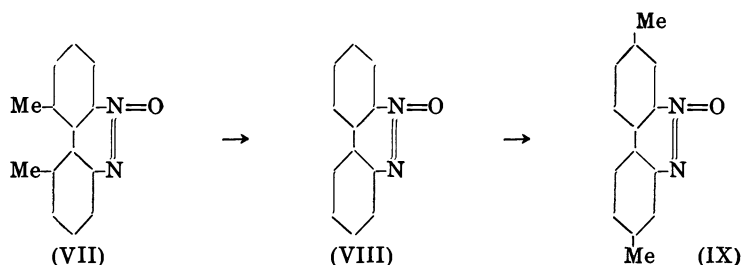
The conversion of 2,2'-dimethyl-6,6'-dinitrodiphenyl (III) into 2,2'-dimethyl-6-amino-6'-nitrodiphenyl (IV) has been effected by Angeletti,⁽⁵⁾ who used alcoholic ammonium sulphide as the reducing agent. It has now been found that this conversion can be accomplished more conveniently by the use of sodium sulphide in place of ammonium sulphide. However, it should be added that sodium sulphide can act in a way other than the above-mentioned partial reduction which occurs when the reaction is carried out under mild conditions. Under somewhat more drastic conditions, there occurs the formation of a cyclic azoxy-compound, 4,5-dimethyl-phenazone oxide (VII), a reaction which recalls the formation of (VIII) and (IX) from 2,2'-dinitro-diphenyl and 4,4'-dimethyl-2,2'-dinitro-diphenyl respectively under similar circumstances.⁽⁶⁾

(3) Meisenheimer and Höring, *Ber.*, **60** (1927), 1433.

(4) Kuhn and Albrecht, *Ann.*, **465** (1928), 282.

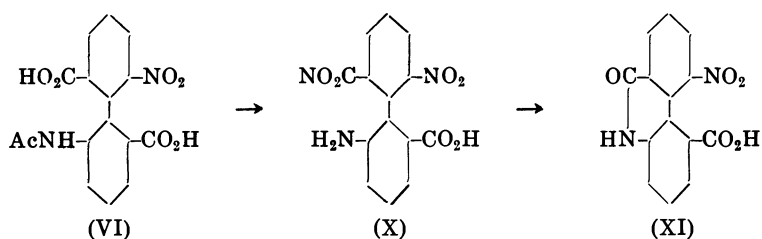
(5) *Gazz. chim. ital.*, **61** (1931), 651.

(6) Ullmann and Dieterle, *Ber.*, **37** (1904), 23.



Attempted resolution of *dl*-6-nitro-6'-acetamidodiphenic acid (VI) with brucine has been fruitless. An almost quantitative resolution, however, has been realized by the use of strychnine, the acid strychnine salt of the *l*-acid and both the acid and neutral strychnine salts of the *d*-acid being obtained easily. The active acids freed from strychnine have $[\alpha]_D = \pm 122.1^\circ$ in a slightly ammoniacal solution. The ammonium as well as sodium salt of the active acids are stable to heat, but the free acids dissolved in concentrated hydrochloric acid appear to racemize even in the cold.

6-Nitro-6'-acetamidodiphenic acid (VI), on heating with sulphuric acid, yields 4-carboxy-5-nitrophenanthridone (XI). The phenanthridone derivative (XI) produced from the active acids has been found to be optically inactive. It has not been possible to isolate the intermediate amino-acid (X), and yet, compared with the formation of the dilactam (I) from 6,6'-diacetamidodiphenic acid which was stated to take place easily, (VI) is converted into (XI) with greater difficulty.



Since the active forms of 6-nitro-6'-acetamidodiphenic acid do not appear stable in the presence of concentrated hydrochloric acid as already stated, the disappearance of optical activity when the phenanthridone derivative (XI) is formed from the active acids in the presence of concentrated sulphuric acid can scarcely be regarded as providing evidence in favour of the coplanar structure for (XI). Nevertheless, it seems not unreasonable to suppose that this question of structure should depend on the

(7) Kenner and Stubbings, *J. Chem. Soc.*, **119** (1921), 593.

size of two atoms which participate in forming a six-membered ring through the 2- and 2'-positions. If the distance between the centres of two atoms in question is smaller than, or nearly equal to, that of the aromatic carbon atoms (1.45Å), as is the case when the atoms are -C-C-, -C-N-, or -N-N-, etc. as in the compounds (I), (II), (VII), and (XI), such a six-membered ring should be uniplanar, for, if so, there is little or no strain. If, on the other hand, it is much larger than 1.45Å as in -S-S- or -As-As-, etc., it is doubtful whether such a compound has normally a coplanar structure, for, if so, it should be accompanied by the production of strain.

Experimental.

(A) Preparation of *dl*-6-Nitro-6'-acetamidodiphenic acid.

2,2'-Dimethyl-6-amino-6'-nitrodiphenyl (IV). This compound has been obtained by Angeletti⁽⁵⁾ by the reduction of 2,2'-dimethyl-6,6'-dinitrodiphenyl with alcoholic ammonium sulphide. The following method, which has been evolved after a large number of comparative experiments, and in which sodium sulphide is employed in place of ammonium sulphide, is not only more convenient but gives a better yield than Angeletti's: a yield of 73 per cent. is obtained by the present method, but 56 per cent. by his method, although allowance has to be made for the unchanged original dinitro-compound which is stated to be recovered to the extent of 33 per cent. by Angeletti's method. Another advantage of the present method is that a large quantity, and indeed any desired amount, of the dinitro-compound can be treated in one experiment with equally good result. The success of the reduction is dependent essentially upon the quantity of the reducing agent and, in a lesser degree, upon temperature, the use of an amount less than given in the direction below leading to incomplete reaction and the use of a more amount at a higher temperature to the production of the cyclic azoxy-compound as described elsewhere.

2,2'-Dimethyl-6,6'-dinitro-diphenyl (136 g.) was dissolved in boiling ethyl alcohol (1300 c.c.) and the solution was allowed to cool. As soon as the temperature reached about 50°C., a solution of Na₂S.9H₂O (240 g.) in water (300 c.c.) previously heated to the same temperature was added with shaking. Some of the separated dinitro-compound disappeared in three to five minutes forming a red solution, meanwhile temperature of the liquid approaching the boiling point of ethyl alcohol. The solution was allowed to stand for an hour or so, at the end of which its temperature was 50°C. Water (450 c.c.) was then added with shaking, when 2,2'-dimethyl-6-amino-6'-nitrodiphenyl began to crystallize at once. The crystals were collected

and washed with a mixture of water and alcohol. The substance weighed 80.5 g. By further dilution of the mother liquor with water (650 c.c.) a second crop melting at 121–123° was obtained, which, on one crystallization from alcohol-water gave a material (9.2 g.) having the same purity as the main crop. The substance thus obtained, as indicated by its melting point (123–124.5°), was almost pure and might be used for further experiments. But it was easily purified by recrystallization from alcohol-water. Then it formed lustrous, yellow, thin plates melting at 124–125° (the m. p. recorded by Angeletti is 122–123°) (Found: C, 69.58; H, 5.87; N, 11.81. Calculated for $C_{14}H_{14}O_2N_2$: C, 69.39; H, 5.83; N, 11.57%). 2,2'-Dimethyl-6-amino-6'-nitrodiphenyl can be distilled under reduced pressure without decomposition.

4,5-Dimethylphenazone oxide (VII). A solution of $Na_2S \cdot 9H_2O$ (5.0 g.) in water (3.6 c.c.) was added to a solution of 2,2'-dimethyl-6,6'-dinitrodiphenyl (1.4 g.) in ethyl alcohol (14 c.c.), and the mixture was heated on the boiling water bath. A vigorous reaction occurred. After 45 minutes' heating, water (6.0 c.c.) was added and the turbid mixture thus obtained, on standing, gave crystalline product (0.43 g.) melting at 151–152.5°C. On crystallization from ethyl alcohol (4 c.c.) it formed yellow needles (0.37 g.) melting at 153°C. (Found: C, 74.8; H, 5.4. Calculated for $C_{14}H_{12}ON_2$: C, 75.0; H, 5.4%).

2,2'-Dimethyl-6-nitro-6'-acetamidodiphenyl (V). 2,2'-Dimethyl-6-amino-6'-nitrodiphenyl (9.7 g.) dissolved in benzene was heated with acetic anhydride (4.4 g.) for 30 minutes. The solution was then shaken with a sodium carbonate solution in order to remove acetic acid formed, and after concentrated greatly, left to crystallize. It was often found necessary to inoculate or to scratch the wall of the vessel to start crystallization. The yield was quantitative. The light yellow needles thus obtained, when dried in an air bath at 60°C., used to begin softening at 83°, and to melt completely at 92°. But on rare occasions, it occurred that they melted sharply at 103–104°C. after the same treatment. The analysis of the lower melting substance indicated that there was one molecule of benzene for two molecules of the acetyl-compound (Found: C, 70.2; H, 6.1. Calculated for $C_{42}H_{42}O_6N_4$: C, 70.6; H, 5.9%). The higher melting form was found to be free from benzene (Found: C, 67.8; H, 5.8; N, 10.1. Calculated for $C_{16}H_{16}O_3N_2$: C, 67.6; H, 5.6; N, 9.9%). The melting point of the lower melting substance did not change after months' standing at ordinary temperature, which showed that the benzene was firmly held. But on keeping it for some time at 80°C., the solvent was removed, the higher melting substance being obtained. A strange incident observed in this connection was that, when the crystals, just after separated from the mother liquor,

were divided into two portions, one half was dried at 60°C. and the other preserved in a vacuum desiccator (4 mm.) at room temperature, it was found that the former, as usual, had m.p. 92°C., while the latter melted sharply at 103–104°C. This phenomenon, however, was not always observed.

dl-6-Nitro-6'-acetamidodiphenic acid (VI). A suspension of 2,2'-dimethyl-6-nitro-6'-acetamidodiphenyl (14.5 g.) in a solution of potassium permanganate (46.0 g.) and crystalline magnesium sulphate (33.0 g.) in water (2000 c.c.) was heated on the boiling water bath with efficient agitation for 2.5 to 3.0 hours, at the end of which the colour of the permanganate disappeared. (When heated without agitation, some of the original compound remained unchanged even after 10 hours, when the permanganate was consumed. Further, when the oxidation was effected by heating over a wire gauze, a trace of the phenanthridone derivative (XI) was produced, an impurity difficult to remove in the later purification work.) The reaction mixture was then cooled, filtered, and the filtrate greatly concentrated in vacuo. After treated with animal charcoal the clear solution was acidified with 50 per cent. sulphuric acid (30 c.c.). The greater part of the product separated at once as an oil which slowly crystallized. The mixture was cooled in ice water for two hours and the solidified mass was collected. For purification, the crude product (15.3 g.) was dissolved in acetone (50.0 c.c.), filtered if necessary, and the solution was mixed with an equal volume of chloroform. Crystallization commenced at once, but it took a long time to complete separation. Thus, almost pure light yellow crystals (13.3 g.) was obtained, but they were once recrystallized from acetone alone. The substance decomposed at 227°C. with darkening after sintering at about 130°C. (Found: C, 55.0; H, 3.9; N, 8.2. Calculated for $\text{O}_{16}\text{H}_{12}\text{O}_7\text{N}_2$: C, 55.8; H, 3.5; N, 8.1%). The *dl*-acid in the purest state, which was obtained from the purified strychnine salts, decomposed however at 229°C. after softening at about 130°C. It is easily soluble in methyl and ethyl alcohols, less so in acetone, and insoluble in chloroform and benzene. It is sparingly soluble in cold water. In boiling water, it is converted though very slowly, into 4-carboxy-5-nitrophenanthridone. This conversion is accelerated by the presence of strong inorganic acids.

(B) Resolution of *dl*-6-Nitro-6'-acetamidodiphenic acid (VI), and its Conversion into 5-Nitrophenanthridone-4-carboxylic Acid (XI). Attempts to resolve *dl*-6-nitro-6'-acetamidodiphenic acid with brucine have not been successful. An easy resolution, however, has been accomplished through the strychnine salts.

Acid Strychnine l-6-nitro-6'-acetamidodiphenate. A hot solution of strychnine (6.68 g.) in chloroform (40 c.c.) was added to a boiling solution of

dl-6-nitro-6'-acetamidodiphenic acid (6.88 g.) in methanol (280 c.c.) and the resulting solution was heated under reflux for 1.0 to 1.5 hours. The acid strychnine *l*-6-nitro-6'-acetamidodiphenate usually began to appear as yellow needles after 20 to 40 minutes' heating. Most of the salt separated while heating, but it was allowed to stand overnight to complete crystallization. As the yellow needles are very difficultly soluble in cold methanol, the *l*-acid present could be separated almost completely in this form, which, after being filtered, could be thoroughly washed with the solvent. (The mother liquor obtained here was used for the separation of the strychnine salts of the *d*-acid as described later.) The yellow needles obtained in this way were found to be so pure that further purification was unnecessary. No change was observed in the melting point (273° with decomposition), in the analytical results, and in the rotation before and after recrystallization from methanol (Found: C, 66.1; H, 5.8; N, 8.4. Calculated for $C_{16}H_{12}O_7N_2 \cdot C_{21}H_{22}O_2N_2$: C, 65.5; H, 5.0; N, 8.3%. Rotation: 0.0226 g. of the substance made up to 15 c.c. with methanol gave $\alpha_D^{20} = -0.22^{\circ}$ for $l = 2$, hence $[\alpha]_D^{20} = -73.0^{\circ}$). To dissolve one gram of the acid strychnine salt of the *l*-acid, it is necessary to boil it with 300 c.c. of methanol for a considerable time. The yellow needles dried in the desiccator somewhat gain weight on exposure to the moist air.

Acid Strychnine d-6-Nitro-6'-acetamidodiphenate. This salt was obtained by concentrating the mother liquor separated from the yellow needles of the acid strychnine salt of the *l*-acid described above. It was often found necessary to inoculate or to scratch the wall of the vessel to start crystallization. It separated usually as crystals free from methanol, but occasionally it happened that crystals containing one molecule of the solvent was formed, which almost completely melted at 175° , where the other showed no change. Both were decomposed, however, at the same temperature, $263^{\circ}C$. They were both nearly colourless, a property in which they differ from the distinctly yellow salt of the *l*-acid. The separation of the acid strychnine salt of the *d*-acid from a methyl alcoholic solution was so sluggish that it was not complete even after leaving overnight, but by evaporation of the solvent on the water bath a greatly supersaturated solution could be obtained, from which the major part of the salt separated fairly quickly on cooling. Crystallized in this way, it formed clusters of almost colourless plates containing no methanol. (The methanol containing substance lost 4.7 per cent. in weight at 80° . Calculated for $C_{28}H_{34}O_9N_4 \cdot CH_3OH$: CH_3OH , 4.5%. Found for methanol-free substance: C, 65.8; H, 5.6. Calculated for $C_{28}H_{34}O_9N_4$: C, 65.5; H, 5.4%. Rotation: 0.0678 g. of substance not containing methanol made up to 15 c.c. with methanol gave $\alpha_D^{20} = +0.33^{\circ}$ for $l = 2$; hence $[\alpha]_D^{20} = +36.5^{\circ}$.)

Neutral Strychnine d-6-Nitro-6'-acetamidodiphenate. As stated above, the crystallization of the acid strychnine salt of the *d*-acid from the methyl alcoholic mother liquor is very sluggish and, moreover, incomplete, a rather large loss of the material being caused. On the other hand, the neutral strychnine salt of the *d*-acid separates from methanol more completely and more quickly, and, therefore, it is better to isolate the *d*-acid in this form. For this purpose, the boiling methyl alcoholic solution (the filtrate separated from the *l*-acid salt) containing the acid strychnine salt of the *d*-acid was treated with a solution of the required quantity of strychnine in chloroform, and the resulting solution concentrated into one-third the original bulk. On cooling, the neutral salt of the *d*-acid appeared in colourless, voluminous needles. In this way, from 6.88 g. of the *dl*-acid, 9.0 g. of neutral strychnine salt was obtained. One recrystallization from methanol (90 c.c.) sufficed to obtain the salt in pure state. It melted at 175° almost completely and decomposed slowly at 207°. It had two molecules of methanol removable by heating at 80°C. (The substance lost 6.2 per cent. in weight at 80°C. Calculated for $C_{58}H_{56}O_{11}N_6 \cdot 2CH_3OH : CH_3OH$, 6.0%. Found for methanol-free substance: C, 68.3; H, 6.1. Calculated for $C_{58}H_{56}O_{11}N_6$: C, 68.8; H, 5.5%. Rotation: 0.1012 g. of substance freed from methanol made up to 15 c.c. with methanol gave $\alpha_D^{20} = +0.16^\circ$ for $l = 2$; hence $[\alpha]_D^{20} = +11.9^\circ$.)

d- and l-6-Nitro-6'-acetamidodiphenic acids. A mixture of 0.1695 g. of the acid strychnine *d*(or *l*)-6-nitro-6'-acetamidodiphenate (corresponding to 0.0860 g. of the free acid) and a slight excess of ammonia was shaken repeatedly with chloroform until the solution was free from strychnine, and the solution was diluted up to 15 c.c. with water. It had $\alpha_D = \pm 1.40^\circ$ for $l = 2$; hence $[\alpha]_D = \pm 122.1^\circ$. The neutral strychnine salt of the *d*-acid (0.1012 g. which contain 0.0344 g. of the free acid) was treated in the same way with aqueous ammonia and chloroform. The solution made up to 15 c.c. gave $\alpha_D = +0.56^\circ$ for $l = 2$; hence $[\alpha]_D = +122.1^\circ$.

The rotation of the active acids had to be examined in the way described above because of the difficulty in isolating the active forms in pure crystalline state. Unlike the *dl*-form, the active forms are very soluble in water and, moreover, when forced to separate from a solution, they tend to form an oil which crystallizes with difficulty. These properties rendered the isolation of the active acids in pure state impossible. Thus, for instance, when a concentrated aqueous solution of the ammonium salt of the active acid, obtained by shaking the strychnine salt with ammonia and chloroform, was acidified with a large quantity of sulphuric acid, only a small portion of the active acid crystallized, which, for the above-mentioned reasons, could not be purified by crystallization.

The decomposition of the ammonium salt of the *l*-acid, obtained by drying its aqueous solution in vacuo, with the calculated amount of oxalic acid in acetone met with rather better success. On mixing an acetone solution of oxalic acid with that of the ammonium salt of the *l*-acid, ammonium oxalate separated, which was filtered off. The filtrate, on concentration followed by addition of chloroform, deposited a small quantity of an oil which, on being left overnight, formed light yellow thin needles (resembling the *dl*-acid in colour) melting at 93°C. with slight decomposition after softening at 85°C. It was readily soluble in acetone and methanol and insoluble in chloroform. It was not quite pure as indicated by the rotation (0.0344 g. of substance made up to 15 c.c. with methanol gave $\alpha_D = -0.33^\circ$ for $l = 2$, while α_D for the *l*-acid, calculated from those of the three strychnine salts obtained under the same conditions as already described, is -0.50°). The yield of the crystals, 17 per cent. of the theoretical, proved, however, to be too small for purification, and the matter was no further pursued.

The active acid appeared to racemize easily in concentrated hydrochloric acid at low temperatures. When a solution of the ammonium salt of the *d*-acid in 5 c.c. of water, obtained from the neutral strychnine salt (3.0 g.), was saturated with hydrogen chloride in a freezing mixture bath, ammonium chloride (0.2 g.) separated first. On filtration, the hitherto yellow solution suddenly turned brown in colour, a small quantity of brownish crystals separating. The brown colour, however, disappeared after a time. Evidently, this must have been the indication that at least a part of the substance had racemized, for the crystals (0.30 g.) collected after some time had α_D in methanol about one-fourth the value expected. The aqueous solution of the ammonium salt of the active acid is stable to heat, no change in optical activity being observed by heating on the water bath for a long time.

5-Nitrophenanthridone-4-carboxylic acid (XI). This substance is produced by heating 6-nitro-6'-acetamidodiphenic acid with sulphuric acid. This change takes place, though not without difficulty, even when an aqueous solution of the diphenic acid derivative is boiled over a free flame in absence of mineral acids. Still, in order to complete the change, the nitroacetamidodiphenic acid has to be heated for a long time with concentrated sulphuric acid. Thus, for instance, when a solution of the diphenic acid derivative in 75 per cent. sulphuric acid was heated on the boiling water bath the crystalline phenanthridone derivative commenced to separate in 30 minutes, but the crystals increased very slowly and the reaction was not complete after 7 hours' heating.

The best yield of the phenanthridone derivative was obtained as follows: a solution of 6-nitro-6'-acetamidodiphenic acid (0.69 g.) in concentrated sulphuric acid (5 c.c.) was heated on the boiling water bath for 8

hours. It was then cooled, diluted with 3.5 c.c. of water (this caused the product to precipitate), and heated again at 100°C. for an hour. After cooling, the yellow powdery crystals were filtered, and washed first with water and then with acetone. The compound does not melt at 330°C. The yield was 0.54 g. or 94.7 per cent. of the theoretical (Found: N, 9.6. Calculated for $C_{14}H_8O_5N_2$: N, 9.8%). It is insoluble or practically insoluble in usual organic solvents. It dissolves sparingly when boiled with nitrobenzene but the solution darkens at the same time. It is soluble in concentrated sulphuric acid and in alkali or sodium carbonate solution. These solutions become gradually dark on standing.

5-nitrophenanthridone-4-carboxylic acid produced from the active 6-nitro-6'-acetamidodiphenic acids was optically inactive.

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LIESEGANG'S STRATIFICATION DEVELOPED IN THE
DIATOMACEOUS GYTTIA FROM LAKE HARUNA,
AND PROBLEMS RELATED TO IT.

By Ken SUGAWARA.

Received July 20th, 1934. Published September 28th, 1934.

Deposits were sampled from Lake Haruna by S. Yoshimura in June, 1932. They were charged in several glass tubes and kept in his laboratory with cork lids. In the course of one year, a series of reddish brown stripes developed in one of these tubes along the glass wall from the surface towards the bottom (Fig. 1). At a glance, they remind of Liesegang's stratification. After the statement of Yoshimura, the stratification had been developed to some extent in March 1933 and it seems to have grown in number downwards thereafter. The author confirmed that this was actually Liesegang's stratification by the measurement of the distance between two succeeding stripes and by the determination of their chemical composition.

The results of the measurement of the distances between succeeding stripes are given in Table 1. In the upper part, the stripes are so densely crowded that they massed into an evenly reddish brown zone and individuals are not able to be discriminated. This part is followed by a series of 16

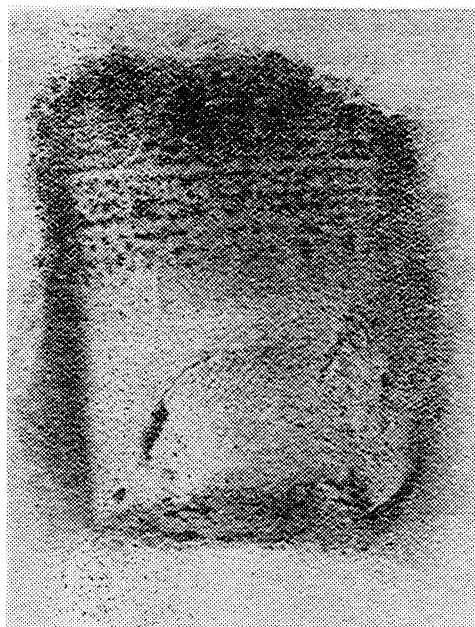


Fig. 1.

distinct stripes. The distance between two consecutive stripes grows as the stripes go downwards. This is what is observed in typical Liesegang's stratification. But there are two irregularities: One lies in that the distance, which grows downwards to the 7th stripes in the section (a), and to the 8th in the section (b), is abruptly somewhat shortened at the succeeding one or two intervals while it continues to grow larger again. The cause of this irregularity is not certain, but it might be attributed to some change of the surrounding condition in the course of the development. The second irregularity is the development of the

Table 1.

No. of stripe	Section a		Section b	
	Depth mm.	Dist. betw. consec. str.	Depth mm.	Dist. betw. consec. str.
I	3.3	}		
II	3.8			
III	4.2	}		
IV	4.6		5.0	
V	5.0	}	5.4	}
VI	5.5		5.9	
VII	6.1	}	6.4	}
VIII	6.6		7.0	
IX	7.0	}	7.4	}
X	7.4		7.8	
XI	7.9	}	8.4	}
XII			8.7	
XIII	8.5	}	9.0	}
XIV	9.2		9.7	
XV		}	10.2	}
XVI	9.9		10.5	

12th and 15th stripes which appear only in section (b), and disappear on the way from the section (b) to (a). Were these two stripes not present, the distance between two succeeding stripes would grow in (b) as regularly as in (a). These two irregular stripes might be independent in their origin of the other ones and they might have been developed secondarily after the completion of the main series. This is what is the case very often in actual Liesegang's stratification. However, as we know nothing about the sequence of the formation of the stripes, this way of interpretation cannot positively be sustained.

As to the comparison of the chemical composition at different parts of the sample, the author performed at first a complete analysis of the lake deposits, results of which are given in Table 2. Then the determination of the content of iron was carried out in three different parts of the sample i.e. in the reddish brown stripes, in the intermediate grey layer, and in the

Table 2.

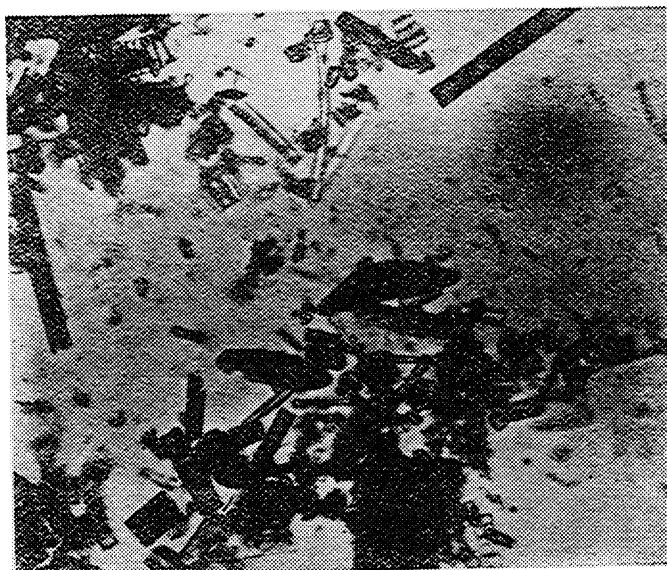
Chemical composition of the deposits dried at 110°C.	
Loss of ignition	16.97%
SiO ₂	62.90
Al ₂ O ₃ }	15.12
Fe ₂ O ₃ }	
(Fe ₂ O ₃)	(3.36)*
Mn ₂ O ₅	0.91
CaO	2.64
MgO	0.03
(P ₂ O ₃)	(0.40)*
	98.97
* determined colorimetrically	

Table 3.

Distribution of iron in the material dried at 110°C.	
	Fe ₂ O ₃
Stripe	10.6%
Intermediate layer	5.6%
Lowest portion with no stripe	1.3%
The iron content was determined colorimetrically	

lowest part where the stratification did not occur, the results of which are given in Table 3. The iron content is 10.6 per cent. in the stripe, 5.6 per cent. in the intermediate layer, and only 1.3 per cent. in the lowest part without stripes, while 3.36 per cent. in the complete analysis, this value lying within the above three. From above analyses, it is obvious that the stripes are mainly composed of iron, which was precipitated presumably in the form of its hydroxide by the reaction between ferrous ion (which was in dissolved state beforehand in the capillary water of the deposits), and the aerial oxygen (which diffused in from the opening of the tube).

The peculiarity of the author's sample lies in that the formation of stripes is due to the oxidation by dissolved gas and in that the medium, in which the reaction occurred, is silicious deposits. In fact, as shown in



Microscopic photograph of the diatomaceous gyttia
from Lake Haruna.

Fig. 2.

Fig. 2, the deposits are a typical diatomaceous gyttia with little contamination, and it seems by its highly developed capillarity to make the diffusion of dissolved gas and ion easy.

As to the mechanism of the development of the stratification little can be told because of the shortage of the facts observed. But taking in consideration that the medium is neutral in reaction and that there is little phosphate, it is probable that at least the greater part of the oxidized iron was coagulated as hydroxide and not as phosphate as it might be the case when the phosphate content were rich.

Now some geological and limnological problems, which are closely related to the stratification dealt above, will be depicted.

1) It is not rare to find examples of a geological specimen which bears a stratification resembling exactly that of Liesegang. But many cases of such a stratification are not accepted as true Liesegang's stratification. They are, except a few examples of igneous rocks such as some species of agate or malachite, mainly developed through the periodic alternation of

sedimenting materials of different natures (such being often the case in examples of sedimentary rocks).

Now in spite of this general scheme, there is one example of sandstone from Münzenberg whose stratification was interpreted as true Liesegang's one by Liesegang⁽¹⁾ himself in 1914 with the following description: "Verschiedene Anzeichen deuten darauf hin, dass es (Eisenhydroxyd, das verschieden dehydriert) vorher einmal in anderer chemischen Verbindung in gleichmässiger Verteilung darin (im Sandboden) vorhanden war. Eine Zeitlang war diese Zone durch überlagernde andere Schichte der Einwirkung der Atmosphärrilien entzogen. Als durch spätere geologische Vorgänge die überlagernden Schichten wieder abgetragen wurden, drangen Sauerstoff, ... von der freien Oberfläche Dabei wurde das Eisen intermediär gelöst; entweder als Ferrosulfat oder als Eisenbikarbonat. Das nachdringende Ueberschuss der Atmosphärrilien verwandelte letztere wieder in unlösliches Eisenhydroxyd." Now when we compare this course of formation of the stratification in Liesegang's sandstone, which is practically based upon his speculation, with that of the example from Lake Haruna, which was established actually half in vitro, both agree in their general scheme, while there is an important difference in nature that, even if the author's example be compacted, it would turn out into a clay-slate-like specimen and not into a sandstone. Anyhow, this agreement may be accepted to be an evidence which strengthens the conviction that true Liesegang's stratification can be formed in natural sedimentary rocks.

2) The second question deals with stratifications which are *to be* found in lake deposits.

After the current opinions, there are two kinds of ways in which a stratification is developed in lake deposits. One is that in which changes of surrounding geological or climatic conditions in a long duration bring forth corresponding changes in the nature of sedimenting materials, and thus a vertical stratification is developed in deposits. The other is that in which the seasonal variation of planctic lives in the lake causes a corresponding variation of sedimenting materials and a vertical stratification is produced, where the portion between two succeeding layers of the same nature corresponds to one year sedimentation. The first example of the stratification of the latter type was given by F. Nipkow⁽²⁾ in 1920 in the deposits of Lake Zürich, which provoked the interest of limnologists with the result that nowadays it is a prevailing tendency to attribute every fine stratification met with to the latter type without enough inspection.

(1) R. Liesegang, *Kolloid-Z.*, **16** (1914), 21-22.

(2) F. Nipkow, *Zeitschrift für Hydrologie*, **4** (1927), 107-143.

Now the author points out other two possible ways in which a stratification can be developed. One is that in which true Liesegang's stratification is developed. Could changes take place in the actual bottom of a lake, as they did in vitro, it is very promising to find Liesegang's stratification in lake deposits. And a lake bears very often the conditions, which favour such changes to take place. For instance, in a large number of lakes in temperate zone, the period of circulation alternates with that of stagnation. In the latter period, which occurs from spring to summer, a high reduction potential is developed in the bottom layer, because of the limited supply of oxygen, and the ferric iron in deposits is easily reduced to diffusible ferrous one. Now the period of circulation, which occurs from autumn to winter, succeeds, in which the surface water, rich in oxygen gets to the bottom and oxygen may diffuse from the surface of the reduced deposits, as it did in the glass tube. Thus the bottom of some lakes bears conditions, which favour the development of true Liesegang's stratification, and this is why the author claims Liesegang's stratification as the third possible type of stratifications in lake deposits.

The fourth stratification type of lake deposits is also thinkable. Such a view is based upon the above observation that the diffusible iron is heavily adsorbed on the surface of the deposited one and the iron, which was evenly distributed beforehand, is now concentrated locally at a particular point, where it is precipitated by oxidation (see Table 3).

Thus, in the period of circulation, as the iron, present on the deposits surface, is oxidized and precipitated there, ferrous iron moves by diffusion from deeper layer towards the surface to be accumulated there.

In consequence, be such a sequence of changes regularly repeated, it is highly possible that an annual stratification is developed in which layers rich and poor in iron alternate and to which the author gives the name "the fourth possible type of stratification in deposits".

Finally it must be remarked also that there exist moments which act negatively upon the formation of these stratifications or act destructively upon the stratifications once developed. As an example of the former moment, the so-called "Mikroschichtung" may be mentioned, and as that of the latter the movement of some of benthic animals in the deposits. Such circumstances might be given as the answer why it is not so easy to find examples of the stratifications discussed above.

3) The final problem is related to the redissolution of precipitated iron. As to its fate, iron differs from other elements in lake deposits in that it is favoured to be accumulated upon the surface of deposits as stated above.

There is another important difference between them. The iron, which is accumulated upon the surface as mentioned above, tends to be reduced into

(2) An evidence is given which strengthens the conviction that true Liesegang's stratifications can be found in natural sedimentary rocks.

(3) It is pointed out that there are two kinds of ways possible, besides those hitherto established, in which stratifications are developed in lake deposits.

(4) The cycle of iron in a lake is dealt, and a reasoning is given, which supports the view that a considerable portion of the deposited iron is redissolved and is carried back to the main water.

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THE COLLOIDAL BEHAVIOUR OF SERICIN. V.*

By Hideo KANEKO.

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Sec. XV. The Gelatinization of the Sericin Solution.

A very striking property of certain protein solutions is that they can be transformed into gels. Bogue⁽⁴⁹⁾ assumes that gelatin molecules have tendency to adhere to form long chains, that hydration of these chains takes place, and that when a sufficiently high proportion of water passes from the solution into the threads, gel formation occurs.

One of the chief characteristics of sericin is its power of producing a heat-reversible gel. Silberman states in his book, "Eine sechsprozentige Lösung erstarrt beim Erkalten gallertartig, obwohl sie bereits bei einem Gehalt von 1% gelatiniert. Die Erstarrungsfähigkeit wird indessen durch langes Kochen aufgehoben."

On cooling a moderately strong sol of sericin, it sets to a jelly, which is reconverted into sol on warming. This change does not take place at a definite temperature, for the process is continuous as is shown by the cooling curve. Agglomeration is negligible in comparison with the degree of hydration of sericin micellæ, so it is apt to form a clear jelly.

* Continued from p. 352 of this volume.

(49) Bogue, *J. Am. Chem. Soc.*, **44** (1922), 1343.

On adding some electrolytes it forms an opaque cloudy jelly, for its agglomeration is raised by it. This gelatinization may be due to increase of its hydration following the decrease of charge on sericin micellæ.

The sericin sol obtained from cocoons having good "kaijo" forms a jelly more easily than that obtained from cocoons having bad "kaijo." This may be due to the difference in hydration and form of sericin micellæ. The nonspherical colloid particles are, in general, apt to gelatinize more easily than the spherical⁽⁵⁰⁾.

(1) **Effect of Concentration of Sericin on Gelatinization.** A gelatin sol of 0.25 per cent. does not gelatinize at room temperature. In 1929 S. Bito and N. Oku⁽⁵¹⁾ found that the sericin solution of 0.1 per cent. can form gel after a considerably long time at room temperature and that the sol-gel transformation is reversible. I measured the degree of gelatinization of sericin solutions by the angle of inclination of the test tube containing the sericin gel just when the surface was observed to move, and by the height of liquid raised in a capillary tube having an inner diameter of 0.18 mm. when the end of the capillary tube was brought in contact with the surface of the gel. The results are shown in Table 76.

Table 76. For good "kaijo" (at 15°C.)

Conc. of sericin (%)	Angle of inclination of the test tube (degree)		Height of liquid in the capillary tube (mm.)	
	2 hr. later	18 hr. later	2 hr. later	18 hr. later
0.88	91	above 90	2.0	1.8
0.73	70	„ 90	2.1	2.0
0.66	62	94	2.1	2.0
0.58	50	84	2.2	2.1
0.44	35	63	2.4	2.3
0.35	23	50	2.6	2.5
0.29	20	41	2.7	2.7
0.176	20	23	3.1	3.0
0.088	20	20	3.3	3.2

The rate of gelatinization of the sericin solution depends on the pH value of the medium. At the isoelectric point of sericin, the solution tends to set into a gel easily, for the charge on the sericin particle is the least. The influence of pH on the gelatinization of the sericin sol is shown in Fig. 34.

(50) S. Praksh, *J. Ind. Chem. Soc.*, **9** (1932), 193.

(51) S. Bito and M. Oku, *Reports Gunze Phys. Chem. Lab.*, 1929, No. 4, 10.

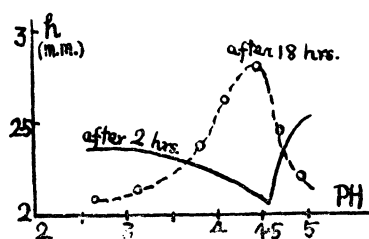


Fig. 34.

The height of liquid raised in the capillary tube was minimum near pH 4.5 after two hours; so pH 4.5 may correspond to the isoelectric point of sericin. When the rate of gelatinization becomes greater, the cloudy, milky gel sets and easily a syneresis takes place in the range of pH 3.5-4.8. So the height of liquid had a maximum value near the isoelectric point

of sericin because of syneresis developed after 18 hours.

(2) **The Change in pH during the Gelatinization.** During gelatinization, the pH of the sericin solution generally increased at first, reaching a maximum point after a few hours, then fell gradually, and a syneresis took place (Table 77 and Fig. 35).

Table 77.

1.18% (Good "kaijo"), 18°C.

Time	pH
30 min.	5.61
60 "	5.71
90 "	5.80 (greatly gelatinizes)
120 "	5.84
180 "	5.67
300 "	5.16
360 "	5.10
30 hr.	4.41
48 "	4.19 (syneresis)

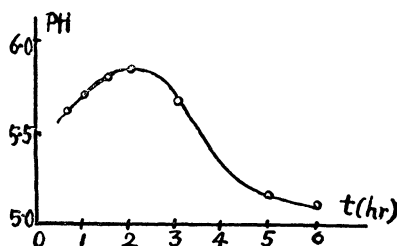


Fig. 35.

(3) **Effect of Time of Heating on Gelatinization.** Prolonged heating at 100°C. caused lowering of viscosity, gradual loss of sensitiveness to electrolytes, and an increase in cataphoretic velocity. At the same time the solution became clear gradually and refused to gelatinize again at room temperature. These may be due to the disintegration of sericin micellæ into smaller units and the decrease in their hydration.

It is obvious that pH of the sericin gel increases with increasing time of heating, and that longer time is necessary to form a stiff gel.

(4) **Effect of Ultra-Violet Ray on the Sericin Gel.** On exposing a sericin solution to ultra-violet ray radiated from a mercury lamp, it became remarkably clear, and its viscosity diminished, and further difficulty in gelatinization was caused by heat. The cause may be attributed to the decrease of the size and hydration of sericin particles.

(5) **Cooling Curve of the Sericin Gel.** I cooled down the sericin sol from 80°C. in a cooling apparatus and obtained a cooling curve following Fisher's formula :

$$\log (T-T_e) = \log (T_a-T_e)-at,$$

where T_a , T_e and T are respectively initial, end, and arbitrary temperatures, and a is constant for sol or gel.

It is clear that $\log (T-T_e)$ is a linear function of time t . But in the case of transformation from sol into gel, the heat of gelatinization is evolved, so the cooling curve shows a sudden change at about 50°C. (Table 78 and Fig. 36).

Table 78.

Conc. %	Temp. at B
0.80	43.2
0.85	46.6
0.91	50.1
1.02	55.6

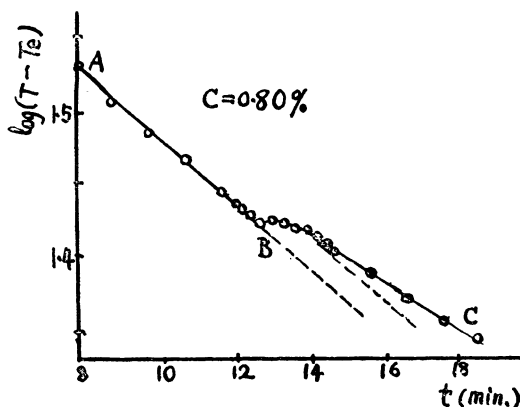


Fig. 36.

The temperature of the sudden change was raised with increasing concentration of the sericin solution. And in low concentrations the temperature, at which the cooling curve bent, was proportional to the concentration of the sericin sol, and the sericin solution might be able to set to a gel at temperatures from 40°C. to 50°C. after a long time. Near this point the variation of the surface tension of the sericin solution with time of standing was very remarkable as already stated.

The values of constant α are on an average 0.022 for the sericin sol and 0.0195 for the sericin gel. The constant α is equal to $E/C\rho$, where E is a cooling factor, C and ρ are respectively the specific heat and the density of sericin.

So I can presume that the conductivity of heat in the sericin sol is greater than that in the sericin gel. If the specific heat of the sericin gel be 0.389, that of the sericin sol may be 0.350.

(6) **Effect of Temperature on the Setting of Gel.** On standing at various temperatures for two hours, sericin solutions gave the results shown in Table 79 in gelatinization.

Table 79. [Cf. (1) of this Section.]

Temp. (C.)	19	30	40	50	60	70
Angle of inclination of the test tube (degree)	180	180	180	165	90	70
Height of liquid in the capillary tube (mm.)	2.0	2.05	2.05	2.15	2.5	2.6

Near the temperature 55°C., the angle of inclination and the height of water raised in a capillary tube showed remarkable changes, and it is considered to be due to sol-gel transformation which can be found in most organic gels and in some inorganic gels, such as thorium arsenate, V_2O_5 , mercurisulpho-salicylic acid. The time of setting is generally decreased as the temperature is raised. At low temperatures sericin micellæ can form larger molecular aggregates and their hydration is increased.

(7) **Softening Point of the Sericin Gel.** With respect to sol-gel reversibility, it must be remarked that the temperature of initial gelatinization and that of melting are never quite the same. Some examples are given in Table 80.

Table 80.

	Setting-temp.	Melting-temp.
4% Gelatin sol	28°	31°
4% Agar-agar sol	40°	85°

The test tube, containing a stiff sericin gel and having a connecting narrow glass tube through the stopper, was inverted ver-

tically in water and then it was heated, the temperature being raised at the rate of 0.5° per minute. The temperature at which the gel is softened and falls down is called the softening point of the gel. The results are given in Table 81.

Table 81.

Good "kaijo"		Mid. "kaijo"		Bad "kaijo"	
Conc. (%)	Soft. p. (C.)	C (%)	S. p. (C.)	C (%)	S. p. (C.)
0.915	89.1	0.84	83.2	0.77	74.1
0.85	85.5	0.72	76.1	0.70	70.0
0.78	83.0	0.615	69.0	0.62	64.5
0.60	75.0	0.54	65.5	0.51	59.0
0.40	60.1	—	—	—	—

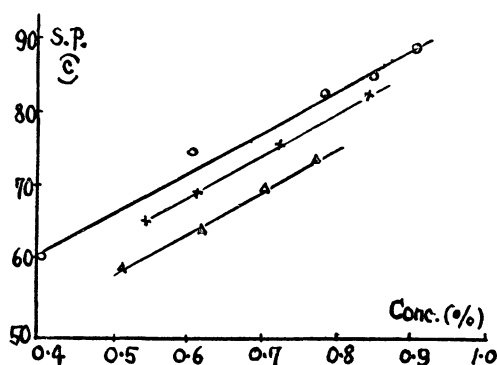


Fig. 37.

As shown in Fig. 37, the softening point of the gel was proportional to the concentration of the gel in such low concentrations.

The softening temperature varied with different "kaijo" of cocoons. The sericin gel obtained from cocoons having good "kaijo" had a higher softening point than that obtained from cocoons having bad "kaijo".

(8) **Reversible Sol-gel Transformation.** On cooling the sericin solution, the sol-form sets to a gel-form and the latter was reconverted into the sol-form on warming.

(a) **Effect of Redissolution.** The sericin gel became reversible to the sol on warming above 60°C . Such a re-dissolved sol sets again to a gel on cooling after a considerable time.

(b) **Effect of Shaking of the Gel.** When the sericin gel was shaken strongly, it transformed imperfectly into a sol which was reconverted into a gel after a long time. That was caused by a thixotropic property of the sericin gel.

(9) **Effect of the Other Substances on Gelatinization.** In general, the rate of gelatinization is accelerated by the addition of a small amount of acids or salts, and retarded by the addition of bases (Table 82). The action of acids and alkalis is the most important factor.

Table 82.

	Gelatinatization	
	accelerated by	retarded by
Acids	HCl, H ₂ SO ₄ , CH ₃ CO ₂ H, Tartaric acid, Malic acid. Citric acid, Succinic acid. Phthalic acid, etc.	Carbonic acid. Oxalic acid, Glycocoll,
Bases	—	NaOH, KOH, NH ₄ OH
Salts	(NH ₄) ₂ CO ₃ , Na salts	—
Organic Matters	Glycerin, Mannite, Glucose, Cane sugar, etc.	Alcohols (in very low conc.)

From the obtained results it can be noticed that the sodium salts accelerate gelatinization in accordance with Hofmeister's lyotropic series in low concentration: $I > NO_3 > \text{tatrte} > Cl > \text{acetate} > PO_4 > SO_4 > \text{oxalate}$. The salts which lead to swelling and hydration of the sericin micellæ, affected the rate of gelatinization acceleratively.

From stabilizing electrolytes, the ions carrying the same charge are adsorbed. By increasing the concentration of such electrolytes, the time of setting of the gel increases, and agglomeration tendency decreases.

Sec. XVI. Freezing of the Sericin Solution.

On freezing a sericin solution, sericin precipitated in form of fibers which were only incompletely soluble on thawing. In the case of a certain protein, the dispersed phase, protein particles, changes its colloidal property on freezing and can not be converted again into colloidal sol state by melting. The sericin solution was frozen by cooling in the freezing mixture at -6°C . for two hours and then left to stand at room temperature overnight. The two components of sericin behaved differently on thawing: the fibrous precipitate which consisted probably of sericin A did not re-dissolve while the other did. This difference may be employed for the separation of sericin A and sericin B in low concentration. The proportion of these two components of sericin separated by freezing are shown in Table 83.

From Table 83 it can be seen that the proportion between irreversible and reversible sericins varies remarkably with "kaijo" of cocoons and that these results are nearly coincident with those obtained by the precipitation with ammonium sulphate. The amounts of irreversible sericin, sericin A,

Table 83.

“Kaijo”	Conc. of sericin (%)	Quantity of solution taken (g.)	Irreversible sericin		Reversible sericin	
			(g.)	(%)	(g.)	(%)
Good	0.958	9.883	0.075	78.12	0.021	21.87
	0.710	9.912	0.057	79.16	0.015	20.83
	0.500	9.967	0.037	75.51	0.012	24.49
Middle	1.10	9.984	0.066	58.92	0.046	41.07
	0.750	9.932	0.042	56.00	0.033	44.00
	0.605	9.950	0.032	53.33	0.028	46.66
	0.483	9.879	0.025	51.02	0.024	48.97
Bad	1.076	9.982	0.046	42.59	0.062	57.40
	0.880	9.968	0.036	40.90	0.052	59.09
	0.590	9.985	0.023	38.98	0.035	59.32

increases with increasing concentration of sericin, but in high concentrations it tends to coagulate together with a small quantity of reversible sericin.

Table 84.

Conc. of sericin (%)	Content of N (%)	
	Irrev.	Rev.
0.20	16.40	16.05
0.36	16.35	15.95
0.60	16.30	15.55
0.74	16.26	15.40

The isoelectric point of irreversible sericin in 0.1 N NaOH was nearly at pH 3.89.

The nitrogen contents of irreversible and reversible sericins from cocoons of good “kaijo” are shown in Table 84.

It is noticed that the nitrogen contents of irreversible and reversible sericins obtained from the dilute solution are approximately equal to those of sericin A (16.36%) and sericin B (16.11%) respectively. At high concentration separation of the two components is incomplete as already described, and at the same time the decomposition of sericin micellæ may probably

occur on freezing. T. Tadokoro found that the nitrogen content of frozen orizenin was less than that of the original substance.

(1) **The Frozen Sericin and Bound Water.** The coagulated irreversible sericin contains a small amount of bound and capillary water. The sericin was separated from the liquid by filtration and, after adhering water was removed with dry filter paper, it was dried in a steam bath. The results given in Table 85 were obtained for good “kaijo”.

If the percentage of the water content be denoted by P , and that of the irreversible sericin by S , then P is a linear function of S :

Table 85.

Conc. (%)	Water content		Irreversible sericin (%)
	(g.)	(%)	
0.958	0.650	6.64	78.12
0.71	0.607	6.17	79.16
0.50	0.510	5.14	75.51

$$P = bS - a,$$

where a and b are constants. Constant a depends on the "kaijo" of cocoons, and the better the "kaijo," the greater its magnitude. Constant b is universal for sericin and about 0.24.

(2) Freezing Point Depression of the Sericin Solution.

(a) **Non-dialysed Sericin Solution.** Freezing point depression of sericin solutions obtained for good "kaijo" by the usual physico-chemical method are shown in Table 86. P denotes the osmotic pressure in atmospheres calculated from the following formula:

Table 86.

Conc. (%)	Δ (C.)	P (atm.)	Δ_a	Bound water (%)
0.08	0.001	0.00125	2.188	3.55
0.23	0.005	0.00625	2.210	4.25
0.36	0.008	0.0100	2.229	4.90
0.45	0.010	0.0125	2.245	5.39
0.59	0.017	0.0212	2.265	5.87
0.67	0.022	0.0275	2.280	6.24
0.75	0.025	0.0312	2.295	6.68
0.85	0.033	0.0412	2.305	6.75
0.92	0.038	0.0475	2.315	6.93
1.06	0.052	0.0650	—	—

$$P = 1.25\Delta \text{ (at } 15^\circ\text{C.)},$$

where Δ is the freezing point depression of the sericin solution. To a sericin solution containing exactly 10 grams of water, 0.01 mol of sucrose was added, which, if all of the water were free to dissolve sucrose, should form a molar solution. The freezing point depression (Δ_a in Table 86) of the sericin-sucrose solution was measured, and the depression in the freezing point due to the added sucrose was thus

determined. The molecular constant for the depression of the freezing point was taken as 2.10° instead of the usual value 1.86° , inasmuch as sucrose forms a hexahydrate in solution. If less than 10 grams of water is free to dissolve sucrose, the depression of the freezing point due to the addition of the sucrose will be greater than expected theoretically.

Accordingly, if $\Delta_a - \Delta$ is greater than 2.10° , a direct proof is obtained that 10 grams of water was not all free to dissolve sucrose, and the value of the excessive depression is directly related to the amount of bound water. Thus one mol of sucrose dissolved in 1000 grams of water combines with 6 mols of water, and we have, theoretically, one mol of sucrose hexahydrate dissolved in $1000 - (18 \times 6)$ or 892 grams of water, which gives a depression of 2.1° . Therefore, the percentage of bound water equals,

$$\frac{\Delta_a - (\Delta + 2.10)}{\Delta_a - \Delta} \times 89.2.$$

The freezing point depression of the sericin solution (Δ) is approximately proportional to the concentration when the latter is small, but it increases much more rapidly than concentration when high. This may be chiefly due to the increase of electrolytes and the decrease of adsorption of sericin micellæ.

The bound water of sericin calculated from the above formula varied with the concentration of sericin and also with the pH of the solution.

At the same concentration, the freezing point depression of the sericin solution obtained from cocoons having bad "kaijo" is greater than that obtained from cocoons having good "kaijo." This was coincident with the experimental results of electrical conductivity.

Table 87.

Conc. (%)	Δ (C.)	P (atm.)	Δ	Bound water (%)
0.12	0.004	0.0050	2.205	4.09
0.20	0.006	0.0075	2.222	4.67
0.22	0.007	0.00875	2.225	4.74
0.27	0.009	0.01125	2.245	5.42
0.40	0.015	0.01875	2.275	6.31
0.45	0.018	0.02250	2.315	7.11
0.67	0.033	0.04125	2.425	10.89
0.80	0.046	0.0575	2.495	12.71

(b) **Dialysed Sericin Solution.** The results obtained for the sericin solution dialysed for two days are given in Table 87. For the solution containing less than 0.3 per cent. sericin the osmotic pressure was nearly proportional to the concentration of sericin. Table 88 shows the molecular weights of sericin calculated from Morse's equation :

$$M = \frac{C}{P} \times RT,$$

Table 88.

	Sericin (g./100c.c.)(C)	$\frac{C}{P}$	Mol. weight (M)
Nondialysed sericin	0.08	64.0	15050.24
	0.23-0.45	36.2	8935.80
Dialysed sericin	0.20	26.7	5855.0

where M is the molecular weight of dry sericin, P osmotic pressure in cm. of water of density 1, C concentration of the dry protein in g. per 100 c.c. of the solvent, R the gas constant, and T absolute temperature.

The molecular weight of sericin is really much greater than these values and it would probably be in the order of ten thousand.

Sec. XVII. Some Properties of Sericin Gel.

(1) **Precipitation of Sericin in an Electric Field.** When two platinum electrodes a few centimeters apart were dipped in sericin gel and an electrical field was established in it by connecting the electrodes with the terminals of a direct current, sericin began to coagulate in a ring form around the anode after a few minutes, and gradually larger similar zones were produced outside the first one as shown in Fig. 38. In some cases sericin coagulated in fibrous form near the middle between the two electrodes.

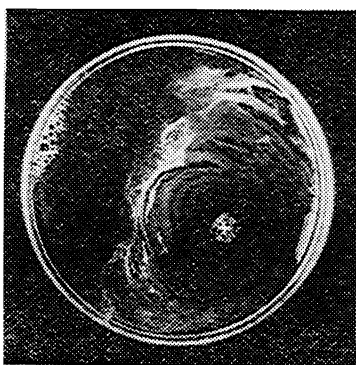


Fig. 38.

When a drop of congo red solution was added to the sericin solution before gelatinization and an electric current was passed through the gel, it turned red near the cathode and blue near the anode,

The flocculation of sericin preceded naturally the syneresis of gel zones and the flocculated sericin consisted probably of sericin A.

When small amounts of salts of alkaline earth and earth metals such as $MgCl_2$, $AlCl_3$, $Al(NO_3)_3$, or salts of heavy metals such as $NiSO_4$, $FeSO_4$, $SnCl_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, were added to sericin gel, the

rythmical rings were produced around the cathode on passing an electric current through the gel. The formation of such rings may be due to the coagulation of sericin caused by the action of the cations of these salts.

Salts of alkali metals such as NaCl , KCl , NH_4Cl , sodium acetate, KMnO_4 , ammonium molybdate, and organic matters such as urea, glucose, resorcinol, allantoin, have no effect on the formation of rings around the anode. Considering from these facts, it is probable that salts of magnesium, aluminium, and heavy metals are contained in neither the sericin gel nor the sol.

(2) **Liesegang's Phenomena in the Sericin Gel.** Under suitable circumstances, a precipitate formed by diffusion of reacting solutions into a gel may be deposited in a number of rythmical bands or layers such phenomena were first observed by Liesegang in 1896.

Liesegang's phenomena in the sericin gel were first noticed by S. Bito and M. Oku⁽⁵²⁾ in 1929 and they investigated the rythmical precipitation of silver chromate, magnesium hydroxide, and lead iodide.

I also studied the same problem and obtained some rythmical precipitates. The sericin sol containing minute amount of potassium dichromate and sodium citrate was gelatinized in three hours at room temperature and a drop of a 10 per cent. silver nitrate solution was allowed to diffuse into the gel overnight. Silver chromate precipitated in a series of concentric rings. By the addition of one drop of silver nitrate solution in sericin gel, the rythmical rings were produced in the presence of the following substances:

Inorganic substances such as $\text{K}_2\text{Cr}_2\text{O}_7$, K_2CrO_4 , AlCl_3 , FeSO_4 , MgO , borax, ammonium molybdate, etc.;

Organic substances such as phthalic acid, glycine, pyrogallol, diphenylamine, sodium salicylate, ammonium oxalate, etc.

(3) **Diffusion in the Sericin Gel.** A test tube was filled one-third with a sericin sol. After the sol solidified to a jelly the solution (5 c.c.) to be investigated was poured upon it, and the test tube was placed in a thermostat. After a day, the supernatant fluid was decanted from the jelly. The jelly was examined on the progress of diffusion by means of a cathetometer after 6 hours and 30 hours (Table 89 and 90). In order to compare with the diffusion in other jellies, I also determined the diffusion in gelatin and agar jelly of the same concentration. In the same concentration, diffusion of dyestuffs in the sericin gel was slower than in agar or gelatin gel. Moreover, the order of velocities of diffusion was not quite the same in agar or gelatin as in sericin: Bismarck brown < malachite green < methyl violet < quinoline yellow < rhodamine G. < congo red < eosine, in agar or gelatin.

(52) S. Bito and M. Oku, loc. cit.

Table 89.

Diffusion of inorganic salt solutions into sericin gel. (cm./day)
(Conc. of salt solutions, 1 N ; temperature, 10.0°C.)

Salt \ Sericin	0.45%	0.58%	0.67%	0.72%	0.84%	0.96%
K ₂ Cr ₂ O ₇	0.35	0.33	0.32	0.33	0.21	0.20
KMnO ₄	0.72	0.72	0.65	0.62	0.50	0.34
CuSO ₄	0.85	0.85	0.83	0.83	0.73	0.45
K ₂ CrO ₄	1.00	1.02	0.97	0.95	0.95	0.65
Cu(CH ₃ CO ₂) ₂	1.19	1.12	1.09	1.04	1.00	0.85

Table 90.

Diffusion of dyestuff solutions into sericin gel. (cm./day)
(Conc. of dyestuff solutions, 0.1% ; temperature, 10°C.)

Dyestuff \ Sericin		0.56%	0.58%	0.66%	0.69%	0.80%
I	Bismarck brown	0.10	0.10	0.0	0.0	0.0
	Methyl violet	0.20	0.20	0.15	0.10	0.08
	Malachite green	0.25	0.25	0.25	0.23	0.13
	Quinoline yellow	0.30	0.30	0.30	0.28	0.22
II	Congo red	0.45	0.40	0.30	0.30	0.28
	Rhodamine G.	0.60	0.45	0.35	0.33	0.30
	Eosine	0.65	0.60	0.40	0.38	0.35

(To be continued.)

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH.
VI. THE ACTION ON CYCLOHEXYLAMINE
AND ITS DERIVATIVES.*

By Harushige INOUE and Koshiro ISHIMURA.

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Cyclohexylamine as well as chloro- and iodo-cyclohexanes, when heated with hydrogen iodide in a sealed tube at 200° for several hours, produces methylcyclopentane.⁽¹⁾ One of the authors has previously⁽²⁾ observed that cyclohexanol and its derivatives are converted chiefly into methylcyclopentane and its derivatives respectively by the catalytic action of Japanese acid earth heated at 300° under ordinary pressure, while at 200° they are mainly converted into cyclohexene and its derivatives respectively.

The present experiments were undertaken to ascertain whether cyclohexylamine and its derivatives also undergo the same isomeric change from the six-membered carbon rings to the five-membered ones by the contact action of the acid earth.

The amines used in the experiments were prepared from the corresponding phenols; pure carbolic acid and three isomeric cresols were reduced to hexahydrophenols by Sabatier and Sendrens's method, which were then oxidized with chromic acid, and the resulting ketones were changed into their oximes, from which the required amines were obtained by the reduction with metallic sodium and absolute alcohol. At every stage of the preparation, care was especially taken for purification, all the specimens being therefore very pure and entirely free from aromatic amines. The catalyst, dried at 300°, filled a glass tube with a length of 1 metre and a diameter of 2 cm., and was heated to 350° electrically, and then the weighed amount of an amine was passed on it. The liquid reaction product was passed through a condenser and collected in a receiver and the escaping gaseous product was bubbled into a series of washing bottles containing normal sulphuric acid to catch ammonia evolved.

* An epitomized translation of the original paper published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Markonikoff, *Ber.*, **30** (1897), 1225; *Ann.*, **302** (1898), 36; *ibid.*, **307** (1899), 336; Zelinsky, *Ber.* **30** (1897), 388. This work was carried out in 1927-1928. Recently Nenitzescu and Cantuniari (*Ber.*, **66** (1933), 1097) observed that cyclohexane is converted into methylcyclopentane when boiled with moist aluminium chloride.

(2) Inoue, *This Bulletin*, **1** (1926), 219; *ibid.*, **9** (1934), 353.

I. **Cyclohexylamine.** The amine (b.p. 134° , d_4^{25} 0.8644, n_D^{25} 1.45757), (26.0 g.), being passed on the earth heated at 350° at the rate of 4.7 g. per hour, yielded 15.5 g. of an oily substance and 3.5 g. of gaseous ammonia. The oil was washed with cold dilute hydrochloric acid to remove basic substances, and then with a dilute soda solution and water, dried over anhydrous sodium sulphate, and thus 13.2 g. of a mixture of hydrocarbons (d_4^{20} 0.8264) were obtained, which, subjected to fractional distillation seven

times, gave the fractions shown in Table 1.

Table. 1.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	$70-76^{\circ}$	1.5	0.7654	1.4233
2	$76-77^{\circ}$	2.0	0.7709	1.4263
3	$77-80^{\circ}$	0.4	0.7741	1.4294
4	$80-85^{\circ}$	0.1	—	—
5	Residue	2.5	0.9213	1.5135

As shown by the physical constants given in the table, the first fraction consists mainly of methylcyclopentane, whose presence was confirmed by the formation of succinic and acetic acids on oxidation according to Aschan.⁽³⁾ As the yield of the fourth fraction was too

small to determine its physical constants, the same experiment was repeated and the fraction with the boiling point $82-85^{\circ}$ was collected, which was found to be almost pure cyclohexene by its physical constants (b.p. $82-85^{\circ}$, d_4^{20} 0.8046, n_D^{20} 1.44466).

The second and third fractions are mixtures of methylcyclopentane and cyclohexene, and the residue is a mixture of higher hydrocarbons, probably the polymers, condensed products, or both, of the above mentioned substances.

The basic substances were, as already stated, separated from the other reaction products by washing with dilute hydrochloric acid. The washing liquid was neutralized with caustic soda and extracted with ether. After the ether was driven off the free amines were weighed (Yield 0.4 g.). The amines were again dissolved in ether and left to stand. Some days after a white crystalline substance deposited on the wall of the vessel containing the ethereal solution, which was identified to be carbazole by its melting point (238°) and also by the characteristic colour reaction. Into the remaining ethereal solution dry carbon dioxide was passed under cooling with ice and common salt, thereby some unchanged cyclohexylamine was thrown down as carbonate. The solution separated from the insoluble carbonate was treated with benzoyl chloride and alkali. The benzoyl derivative pro-

(3) *Ber.*, **31** (1898), 1804.

duced was recrystallized from dilute alcohol and was found to be benzanilide (m.p. 159–160°). The presence of aniline in the basic reaction product was further confirmed by the colour reactions with bleaching powder and with potassium bichromate.

From the above results it may be concluded that ammonia is first split off from cyclohexylamine, cyclohexene being yielded just in the same manner as water is split off from cyclohexanol, and then the resulting cyclohexene undergoes the isomerization from the six-membered carbon ring to the five-membered one producing methylcyclopentane, some polymerization or condensation products being formed simultaneously. The dehydrogenating property of Japanese acid earth is also noticed in the fact that carbazole and aniline are produced.

II. 1-Methylcyclohexylamine-(2). By passing 66.7 g. of 1-methylcyclohexylamine-(2) (b.p. 148–150°, d_4^{20} 0.8639, n_D^{16} 1.45917) on the acid earth heated at 350° at the rate of 3.3 g. per hour, 41.0 g. of an oily substance and 7.8 g. of gaseous ammonia were obtained. From the former 1.0 g. of basic substances was separated in the same manner as in the former experiment and 35.0 g. of a neutral oil (d_4^{20} 0.8066) was obtained, which was fractionated into nine parts after the seventh fractional distillation (Table 2). The parts boiling below 100° were again fractionated three times (Table 3).

Table 2.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 85°	4.2	0.7586	1.4201
2	85–90°	2.0	0.7716	1.4263
3	90–95°	2.5	0.7748	1.4282
4	95–100°	4.9	0.7763	1.4296
5	100–102°	3.8	0.7794	1.4325
6	102–104°	3.1	0.7841	1.4351
7	104–108°	3.9	0.7893	1.4388
8	108–112°	0.7	0.7961	1.4435
9	Residue	7.4	0.9133	—

Table 3.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	70–75°	1.0	0.7492	1.4144
2	75–80°	1.5	0.7630	1.4216
3	80–85°	1.3	0.7686	1.4245
4	85–90°	1.3	0.7727	1.4266
5	90–95°	2.4	0.7750	1.4282
6	95–100°	2.8	0.7776	1.4298
7	Residue	0.7	—	—

The physical constants and the result of elementary analysis of the eighth fraction of Table 2 and the melting point (92–93°) of the nitrosochloride prepared from it by Faworsky and Bergmann's method,⁽⁴⁾ well

(4) *Ber.*, **40** (1907), 4863.

accord with those of Δ^1 -methylcyclohexene. (Found : C, 87.16 ; H, 13.02. Calc. for C_7H_{12} : C, 87.50 ; H, 12.50%.)

From the physical constants it may be safely stated that the fractions boiling between 102° and 108° consist mainly of Δ^2 - and Δ^3 -methylcyclohexenes. A greater yield of the liquid nitrosochloride of bluish green colour is obtained from the lower boiling fraction than from the higher boiling, which shows that the lower boiling parts are richer in Δ^3 -methylcyclohexene, for, according to Markonikoff,⁽⁵⁾ the nitrosochloride of Δ^3 -methylcyclohexene is a bluish green liquid. (The nitrosochloride of Δ^2 -methylcyclohexene is not yet found in literature.)

The fifth fraction of Table 2 (b.p. 100 – 102°), united with the corresponding fraction in another experiment carried out under the same conditions, was treated with concentrated sulphuric acid to remove unsaturated hydrocarbons, and 5.0 g. of the resulting saturated hydrocarbons was fractionated five times over metallic sodium (Table 4).

The physical constants of the first fraction of Table 4 indicate that it is almost pure ethylcyclopentane.

The fifth and sixth fractions of Table 3 (b.p. 90 – 100°) were combined together, treated with concentrated sulphuric acid, and fractionated again over metallic sodium (Table 5).

Table 4.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	90 – 98°	0.4	0.7632	1.4203
2	98 – 100°	1.6	0.7663	1.4221
3	Residue	0.7	0.8667	—

Table 5.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	90 – 96°	0.5	0.7591	1.4177
2	96 – 98°	1.1	0.7621	1.4195
3	98 – 100°	0.8	0.7646	1.4211
4	Residue	1.0	0.8625	—

The physical constants and results of elementary analysis of the first fraction of Table 5 (b.p. 90 – 96°) well accord with those of 1,2-dimethylcyclopentane. (Found : C, 85.49 ; H, 14.60. Calc. for C_7H_{14} : C, 85.71 ; H, 14.29%.) The second fraction (b.p. 96 – 98°) (Table 5) is ethylcyclopentane. (Found : C, 85.56 ; H, 14.47. Calc. for C_7H_{14} : C, 85.71 ; H, 14.29%.)

Ethylcyclopentane thus obtained may be contaminated with a small quantity of methylcyclohexane which is produced from methylcyclohexene by the contact action of concentrated sulphuric acid as one of the authors (H.I.) observed previously⁽⁶⁾.

(5) *Bull. soc. chim.*, [3] **34** (1905), 219.

(6) This Bulletin, **1** (1926), 225.

The first fraction of Table 3 (b.p. 70–75°) is obviously methylcyclopentane. (Found: C, 85.92; H, 14.10. Calc. for C_6H_{12} : C, 85.71; H, 14.29%.)

In order to examine the presence of toluene in the reaction products, the fraction boiling between 108° and 112° (Table 2) was treated with concentrated nitric acid under cooling with ice and salt and then the resulting nitro-compound was reduced with tin and hydrochloric acid. The reduction product showed the colour reaction with β -naphthol, which is characteristic of aromatic amines. It was then converted into a benzoyl derivative and this was recrystallized from alcohol. Its melting point was 130°, identical with that of benzo-*o*-toluide. Toluene was therefore actually present.

Table 6.

Fraction	B.p. (2mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	40–60°	0.4	0.8707	1.4913
2	60–70°	0.5	0.8857	1.4966
3	70–80°	1.2	0.8969	1.5021
4	80–90°	1.6	0.9082	1.5101
5	90–95°	1.8	0.9200	1.5198
6	95–100°	0.5	0.9310	1.5296
7	100–105°	0.3	—	—
8	105–115°	0.2	—	—
9	115–125°	0.8	0.9557	1.5313
10	125–135°	1.6	0.9685	1.5700
11	Residue	1.2	—	—

It was thus possible to detect methylcyclopentane, ethylcyclopentane, dimethylcyclopentane, the three isomeric methylcyclohexenes, and toluene in the neutral reaction product. Methylcyclopentane may here be considered to have been formed not only from cyclohexene but also from ethylcyclopentane by the decomposition analogous to that of ethylcyclohexane into methylcyclohexane⁽⁷⁾. Other hydrocarbons are polymers boiling above 112°. The residue of Table 2 combined with those obtained by other experiments was distilled in steam. Thirteen grams distilled over out

of 17.6 g., the distillate was then twice distilled under the pressure of 2 mm., and the fractions shown in Table 6 were obtained.

The largest portion of Table 6 is the fifth fraction boiling between 90° and 95°, which on analysis gave the following results⁽⁸⁾:

Found: C, 88.42; H, 10.96. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%.

Mol. wt. found: 174. Mol. wt. calc. for $C_{14}H_{20}$: 188.

The acid-soluble reaction product amounted to 1.0 g., from which *o*-toluidine was isolated as the benzoyl derivative, and unchanged methylcyclohexylamine as the carbonate.

(7) Sabatier and Sendrens, *Compt. rend.*, **132**, (1901), 856; *ibid.*, **132**, 1255; *Ann. chim.*, [8] **4**, (1905), 365.

(8) The analysis was carried out after long standing of the sample, so a small amount of atmospheric oxygen seems to have been absorbed by it, some oxidation products being thereby formed.

III. **1-Methylcyclohexylamine-3.** The amine (b.p. 149–151°, d_4^{20} 0.8472, n_D^{20} 1.45357) (68.5 g.) was passed on the acid earth heated at 350° at the rate of 2.7 g. per hour and 34.5 g. of a neutral oil (d_4^{20} 0.8053), 8.5 g. of gaseous ammonia, and 1.4 g. of a basic substance were obtained.

The neutral oil was submitted to fractional distillation seven times over metallic sodium and the fractions shown in Table 7 were obtained. The fractions boiling below 100° were further fractionated three times over metallic sodium (Table 8.) Compared with 1-methylcyclohexylamine-(2), 1-methylcyclohexylamine-(3) produces a much less quantity of the portion boiling below 90°, which in the latter case consists mainly of dimethylcyclopentane as shown by its physical constants and the result of elementary analysis (Found: C, 85.97; H, 14.10. Calc. for C_7H_{14} : C, 85.71; H, 14.29%), but the presence of ethyl- and methyl-cyclopentanes was not definitely confirmed. The physical constants of the third fraction (b.p. 95–100°) of Table 7 are nearly equal to those of methylcyclohexane, which was not confirmed to be present in the reaction products of 1-methylcyclohexylamine-(2). The fractions boiling above 100° consist mainly of three isomeric methylcyclohexenes as in the former case. The nitrosochloride prepared from the

Table 7.

Frac-tion	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 90°	0.3	—	—
2	90–95°	1.7	0.7617	1.4223
3	95–100°	4.7	0.7741	1.4294
4	100–102°	5.5	0.7808	1.4334
5	102–104°	6.9	0.7876	1.4377
6	104–108°	6.5	0.7942	1.4431
7	108–112°	1.2	0.8010	1.4485
8	Residue	5.7	0.9144	—

Table 8.

Frac-tion	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 90°	0.8	0.7552	1.4181
2	90–95°	0.9	0.7660	1.4233
3	Residue	4.1	0.7777	1.4295

Table 9.

Frac-tion	B.p. (5 mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	To 100°	0.4	0.8795	1.4992
2	100–115°	0.7	0.9251	1.5250
3	115–125°	0.4	0.9382	1.5359
4	125–135°	0.8	0.9632	1.5617
5	Residue	0.2	—	—

seventh fraction (b.p. 108–112°) melts at 92°, indicating the presence of Δ^1 -methylcyclohexene, which was further confirmed by analysis. (Found: C, 87.01; H, 12.83. Calc. for C_7H_{12} : C, 87.50; H, 12.50%.) Toluene was again found in the same fraction, which was isolated as benzo-*o*-toluide. (Found: N, 6.48. Calc. for $C_{14}H_{13}ON$: N, 6.63%.) Its amount was,

however, much larger than in the case of 1-methylcyclohexylamine-(2). The residue of Table 7 was submitted to steam distillation, then distilled under the pressure of 5 mm. into the fractions given in Table 9.

In the basic reaction product a trace of *m*-toluidine was noticed together with some unchanged 1-methylcyclohexylamine-(3).

IV. 1-Methylcyclohexylamine-(4). The amine (b.p. 149–151°, d_4^{20} 0.8470, n_D^{20} 1.45157) (110.0 g.) was passed on the earth heated at 350° at the rate of 3.1 g. per hour, and 61.5 g. of a neutral oil (d_4^{20} 0.8049), 12.8 g. of gaseous ammonia, and 1.8 g. of a basic substance were obtained.

The neutral substance gave the fractions given in Table 10 after ten times fractional distillation over metallic sodium.

Table 10.

Frac-tion	B.p.	Yield (g.)	d_4^{25}	n_D^{25}
1	To 90°	0.2	—	—
2	90–95°	0.7	0.7531	1.4187
3	95–100°	2.3	0.7680	1.4253
4	100–102°	3.9	0.7754	1.4299
5	102–104°	10.9	0.7822	1.4335
	104–106°	12.2	0.7840	1.4376
7	106–108°	10.2	0.7948	1.4415
8	108–112°	3.8	0.7970	1.4444
9	Residue	8.0	0.8980	—

Table 11.

Frac-tion	B.p. (5 mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	To 97°	0.5	0.8776	1.4891
2	97–110°	1.2	0.9046	1.5046
3	110–115°	0.7	0.9129	1.5114
4	115–125°	0.8	0.9226	1.5198
5	125–135°	0.7	0.9450	1.5426
6	Residue	0.9	—	—

By the similar treatment of each fraction, three isomeric methylcyclohexenes, dimethylcyclopentane, and toluene were ascertained to occur. In this case, too, the presence of methyl- and ethyl-cyclopentanes was not confirmed.

The residue of Table 10 was distilled under the pressure of 5 mm. (Table 11). The fourth fraction of Table 11 (b.p. 125–135°) was analyzed.

Found: C, 89.38; H, 10.39. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%.

Mol. wt. found: 176. Mol. wt. calc. for $C_{14}H_{20}$: 188.

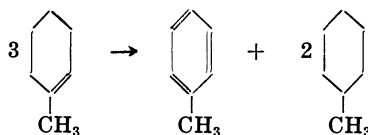
Here again a substance with a probable molecular formula of $C_{14}H_{20}$ was isolated, of which further study was not able to be done on account of the scantiness of the material. In the basic reaction product, *p*-toluidine, unchanged methylcyclohexylamine, and a small quantity of a white crystalline substance melting at 186–190°, probably a homologue of carbazole, were confirmed to occur.

Conclusion.

(1) One molecule of ammonia is first liberated from cyclohexylamine and its methyl derivatives when they are passed on Japanese acid earth heated at 350°, yielding cyclohexene and its methyl derivatives respectively. The molar yield of ammonia produced thereby corresponds to about 80 per cent. of the amine taken.

(2) Some part of cyclohexene thus produced then undergoes an isomeric change from the six-membered carbon ring to the five-membered one giving methylcyclopentane. Methylcyclohexenes suffer the similar isomerization giving ethyl- and dimethyl-cyclopentanes and some part of ethylcyclopentane is further decomposed to methylcyclopentane. The displacement of the double bond within the molecule of Δ^2 - or Δ^3 -methylcyclohexene must occur simultaneously giving Δ^1 -methylcyclohexene, the most stable form of the three isomers, for, in the case of 1-methylcyclohexylamine-(4), Δ^1 -methylcyclohexene can not be otherwise formed.

(3) The acid earth promotes also dehydrogenation, yielding aniline and carbazole from methylcyclohexylamine, and toluene from three isomeric methylcyclohexenes. Toluene is always accompanied by methylcyclohexane, and the yields of the two substances go parallel. The following mechanism may be therefore suggested, which Zelinsky⁽⁹⁾ has proposed for the catalytic reaction of palladium.



The presence of benzene, however, was not confirmed in the reaction product of cyclohexylamine.

(4) Polymerization, condensation, or both, take place at the same time giving polymers or condensed products, whose amounts are about 15–20 per cent. of the total reaction product.

(5) The total quantity of cyclopentane derivatives is much larger in the case of cyclohexylamine than in the case of its methyl derivatives, while of the latter 1-methylcyclohexylamine-(2) gives the largest amount and 1-methylcyclohexylamine-(4) gives the least. It is also observed that the yield of polymers goes parallel to that of cyclopentane derivatives.

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(9) *Ber.*, **57** (1924), 2055.

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH.
VII. THE RELATION BETWEEN THE CONSTITUENTS
OF THE EARTH AND ITS CATALYTIC ACTION.*

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It has been shown in the previous papers⁽¹⁾ that Japanese acid earth has various catalytic actions on various organic compounds. The earth is, however, not a definite compound and it seems most probable that it is essentially a kind of hydrated aluminium silicate mixed with colloidal silica⁽²⁾ and small amounts of many other metallic oxides. Still it remains unknown which of these constituents plays a principal part in its characteristic actions except that it owes its oxidase-like actions to the minute quantity of manganese dioxide contained in it⁽³⁾.

When a mixture of naphthalene and some dry powdered acid earth was heated at about 300° in a sealed tube, a marked amount of a resinous matter was produced, which was found mainly composed of β, β' -dinaphthyl. The rôles played by the chief constituents of the earth in this catalytic action were investigated in the present experiment.

The Resinous Matter. The reaction product in a sealed tube was extracted with benzene. After the benzene was distilled off the residue was distilled in steam to remove unchanged naphthalene, when a mass of chocolate colour was left behind in the distillation flask. About 70 per cent. of this resinous matter passed over between 260° and 310° under 28 mm., and solidified at once to a yellow crystalline mass. It was recrystallized several times from alcohol with the addition of animal charcoal. The colourless scales of β, β' -dinaphthyl were obtained, which melted at 182° when heated alone or with the authentic specimen synthesized from β -chloronaphthalene.

The earth after complete extraction with benzene has a grey colour and its weight increase is always 1-2 per cent. of the resinous matter produced,

* An epitomized translation of the original paper published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue, *This Bulletin*, **1** (1926), 157, 177, 197, 219; **9** (1934), 353; Inoue and Ishimura, *ibid.*, **9** (1934), 423.

(2) Yamamoto, *J. Soc. Chem. Ind. Japan*, **34** (1931), 244 B; *ibid.*, **36** (1933), 38 B, 460 B.

(3) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **33** (1930), 335 B; Iimori, *Bull. Inst. Phys. Chem. Research, Japan*, **9** (1930), 852.

and no other product is found. The yield of the resinous matter depends largely upon the temperature and the duration of the reaction as well as the amount and pre-treatment of the earth, yet it remains constant within about ± 2 per cent. under a definite condition, and it can, therefore, be taken as a direct measure of the catalytic activity of Japanese acid earth on naphthalene.

The Standard Condition. The standard condition to measure the catalytic activity was chosen as follows: 25.00 g. of "pure naphthalene" from Tokyo Gas Co., Ltd. (sulphur content 0.05 per cent.) and 6.25 g. (25 per cent. of the naphthalene) of the dry earth were mixed and charged in a glass tube of 50–70 cm. in length and 2 cm. in diameter. The tube was sealed and heated in an electric furnace. The earth used had been dried at 120° for one hour, powdered, sifted with a sieve of 200 meshes, and heated once more at 300° for one hour. The temperature of the furnace was gradually raised to 300° in the course of just one hour and a half and maintained there for one hour. Then the electric current was cut off and the furnace was left to cool down to room temperature. The content of the sealed tube was washed out with benzene, and filtered by a silk sack. The earth in the sack was then completely extracted with benzene in a Soxhlet apparatus for 8–30 hours. The two benzene extracts were united and filtered, the benzene was distilled off, and the residue was subjected to steam distillation to remove unchanged naphthalene. The resinous matter left behind in the distillation flask was collected, rinsed out with benzene if it stuck to the wall of the flask, in a small weighed beaker, and dried at 120° until a constant weight to 0.01 g. was obtained.

The Relation between the Yield of the Resinous Matter and Chemical Composition of the Acid Earth. Seven specimens of the acid earth were analysed on one hand and their catalytic activities under the "standard condition" were measured on the other hand. The results are shown in Table 1.

No relation between the chemical composition and the catalytic activity seems to be found out from Table 1. But, when we take the ratios of the percentages of other constituents to those of SiO_2 as shown in Table 2, distinct relations between them and the catalytic activities can be found: (1) the larger the value of $\text{Al}_2\text{O}_3/\text{SiO}_2$, the greater the catalytic activity; (2) the larger the values of CaO/SiO_2 and $\text{K}_2\text{O}/\text{SiO}_2$, the smaller the catalytic activity; and, (3) the values of $\text{Ig. loss}/\text{SiO}_2$, $\text{Fe}_2\text{O}_3/\text{SiO}_2$, and MgO/SiO_2 seem to have no relation to the activity.

Table 1.

Earth	Locality of production	Depth of deposit where sample was gathered (metres)	Chemical composition (%)								Yield of resinous matter (g.)
			Ignition loss	SiO ₂	Al ₂ O ₃ ⁽⁵⁾	Fe ₂ O ₃	CaO	MgO	K ₂ O ⁽⁴⁾	Total	
A	Isozawa	7	9.51	65.62	13.61	3.89	1.47	3.98	1.82	99.90	1.65
B	Isozawa	3	7.78	67.91	16.09	3.17	0.60	3.51	1.35	100.41	1.82
C	Itoigawa	6.5	10.45	68.18	14.95	2.53	1.11	1.20	1.02	99.44	1.86
D	Odo-Sekiba	4.5	6.98	72.34	13.73	3.37	1.18	1.28	1.04	99.92	1.90
E	Odo-Sekiba	1.2	8.84	65.69	18.47	2.65	0.79	2.08	1.17	99.69	2.10
F	Itoigawa	Commercial	6.87	67.04	17.71	1.57	0.40	4.99	0.63	99.32	2.23
G	Itoigawa	0.9	11.50	58.92	20.13	3.05	0	3.15	0.95	97.70	2.60

Table 2.

Earth	$\frac{\text{Ig. loss}}{\text{SiO}_2} \times 100$	$\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} \times 100$	$\frac{\text{Fe}_2\text{O}_3}{\text{SiO}_2} \times 100$	$\frac{\text{CaO}}{\text{SiO}_2} \times 100$	$\frac{\text{MgO}}{\text{SiO}_2} \times 100$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2} \times 100$	Yield of resinous matter(g.)
A	14.5	20.7	5.93	2.24	6.07	2.77	1.65
B	11.5	23.7	4.67	0.88	5.17	1.99	1.82
C	15.3	21.9	3.71	1.63	1.76	1.50	1.86
D	9.7	19.0	4.66	1.63	1.77	1.44	1.90
E	13.5	28.1	4.03	1.20	3.17	1.78	2.10
F	10.1	26.4	2.33	0.60	7.44	0.94	2.23
G	19.5	34.2	5.18	0	5.35	1.61	2.60

The problem was then attacked from another side ; each constituent was considered separately and investigated on its catalytic activity for naphthalene.

SiO₂ and Al₂O₃. Silicic acid gel and aluminum hydroxide prepared by various methods were examined in the first place. The results are shown in Table 3.

(4) Na₂O was weighed together with K₂O.

(5) It has been already pointed out by Okazawa that Al₂O₃ content is always larger in the upper layers of Japanese acid earth deposits than in the lower, which may be noticed here again. (*Bull. Inst. Phys. Chem. Research, Japan*, 7 (1928), 977.)

Table 3.

	Method of preparation	Yield of resinous matter (g.)	Remarks
SiO ₂ gel	(a) Dil. solution of Na ₂ Si ₂ O ₅ ·2H ₂ O into 2.8 N nitric acid.	0.03	The quantity of the catalyst, 12.5 g. instead of 6.25 g. Standard condition in other respects.
	(b) Dil. solution of water glass into dil. hydrochloric acid.	0.06	Under the standard condition.
	(c) Ferric chloride solution into water glass solution. (Holmes's gel) ⁽⁶⁾	0.03	„
	(d) Holmes's gel washed with hydrochloric acid.	0.01	„
Al(OH) ₃ ⁽⁷⁾	(a) Clay was treated with sulphurous acid and resulting aluminium sulphite was decomposed by boiling.	0.00	The quantity of the catalyst, 12.5 g.
	(b) Dil. aqueous ammonia into dil. solution of aluminium nitrate.	0.02	Under the standard condition.
	(c) Dil. aqueous ammonia into dil. solution of aluminium chloride.	0.00	„

As shown in Table 3, all the specimens of silicic acid gel and aluminium hydroxide used alone manifest no or quite poor activity. But when the two substances are mixed together in a suitable manner, a remarkable amount of the resinous matter is produced, the activity of the mixed catalyst becoming comparable to that of the acid earth.

Silicic acid gel (a) and aluminium hydroxide (b) of Table 3 are suspended in water separately, about 0.2 g. as SiO₂ or Al₂O₃ being contained per 10 c.c., and the two suspensoids are mixed in a porcelain basin, and evaporated to dryness on the water bath under stirring. The dried mass is powdered, treated as the "standard condition" requires, and tested on its catalytic activity. The yield of the resinous matter produced by the mixed catalyst thus obtained are plotted against the composition of the mixture in Fig. 1. The "standard condition" was adopted in the experiments except that 5.00 g., instead of 6.25 g., of the mixed catalyst was always taken.

Fig. 1 shows that there is a maximum in the catalytic activity in the neighbourhood of the composition, 35 per cent. Al₂O₃ and 65 per cent. SiO₂,

(6) Holmes, *Ind. Eng. Chem.*, **17** (1925), 280; *ibid.*, **18** (1926), 386.

(7) Aluminium hydroxide, as it is very troublesome to wash completely, was finally purified by electro dialysis.

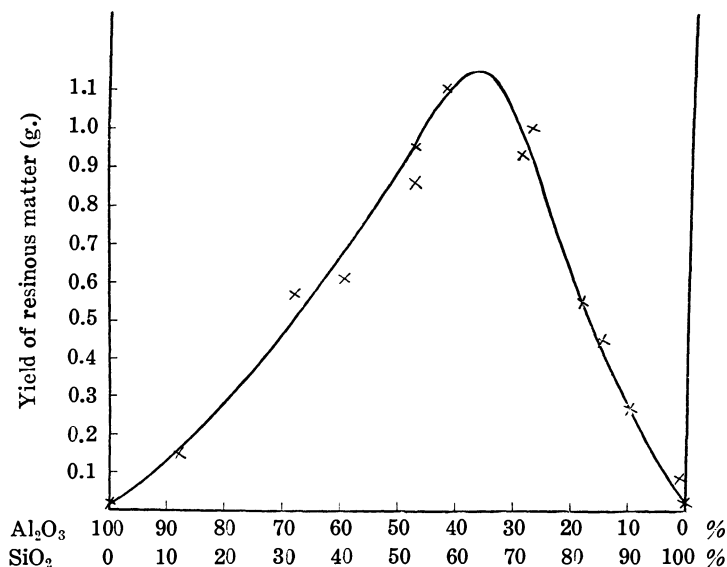


Fig. 1.

which corresponds to $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$. Its position, however, may be shifted according to the method of the preparation of silicic acid gel and aluminium hydroxide and the manner of mixing them. Moreover, it is not explicit whether any definite compound is formed by the simple mixing of the two, and, even if it is actually formed, it cannot be at once taken for granted that its composition and that of the constituent of the acid earth possessing the catalytic activity are identical. Notwithstanding that, it is evident that the co-existence of SiO_2 and Al_2O_3 is essential to the catalysis, and at any rate it is possible to prepare a catalyst with the activity comparable to that of the acid earth by the simple mixing of the above mentioned two substances, each of which is an extremely weak agent for the action when used alone, and the parallelism between the values of $\text{Al}_2\text{O}_3/\text{SiO}_2$ and catalytic activities shown in Table 2 seems to be not unreasonable from the above experimental results.

As already stated, if the acid earth contains free colloidal silica, the catalytic activity of such an earth with a comparatively small content of Al_2O_3 may be raised by adding aluminium hydroxide to it, for catalytically active centres may be newly formed. On the contrary, the addition of silica gel would result only in the dilution of the catalyst and cause the lowering of activity. Experimental results are in close agreement with the above speculation. The acid earth (A) of Table 1 was kneaded with a little water to a paste, diluted with water, and fresh aluminium hydroxide (as

Al_2O_3 about 10 per cent. of the weight of the earth dried at 300°) suspended in water was added to it. The whole was then evaporated to dryness on the water bath under stirring. This mixture used under the "standard condition" yielded 1.95 g. of the resinous matter. The increase in the yield of the product is about 20 per cent. (refer to Table 1 and 2). By the similar treatment the activity of the acid earth (C) of Table 1 was raised by about 15 per cent., whilst it was lowered by about 6 per cent., when the earth was mixed with silica gel (10 per cent. as SiO_2).

Hydroxides of Alkali and Alkaline Earth Metals. As stated above, the larger the ratios CaO/SiO_2 and $\text{K}_2\text{O}/\text{SiO}_2$ the smaller is the catalytic activity. It seems very probable, therefore, that the hydroxides of alkali and alkaline earth metals behave as poisons to the catalysts, and, as a matter of fact, this was the case. To the acid earth (F) of Table 1, a dilute solution of sodium hydroxide was added and the whole was evaporated up under stirring. Under the "standard condition" this contaminated catalyst gave no resinous matter when the quantity of the added hydroxide amounted to 5 per cent. of the weight of the dry earth, the catalytic activity being thus destroyed entirely, while the depression of the activity was 10 per cent. on the addition of 1 per cent. of the hydroxide. The acid earth (E) mixed with 3 per cent. of sodium hydroxide gave only 0.03 g. of the resinous matter (the depression is more than 98 per cent.). Potassium hydroxide is a stronger poison; with 1 per cent. of the hydroxide the activity of the earth (D) was lowered by about 20 per cent.

The action of the hydroxides of alkaline earth metals is milder; the acid earth (F) with 5 per cent. (as CaO) of calcium hydroxide gave 0.24 g. of the resinous matter, the depression of the activity being about 90 per cent., and with 3 per cent. of CaO the activity of the acid earth (F) was lowered by about 50 per cent. The intensity of the poisoning by barium hydroxide is nearly equal to that by calcium hydroxide.

It was further observed that, when the poisoned earth was treated with hydrochloric acid, it recovered the original activity completely.

Ferric and Magnesium Hydroxides. As seen from Table 2, the value of neither $\text{Fe}_2\text{O}_3/\text{SiO}_2$ nor MgO/SiO_2 has parallelism with the catalytic activity. It may be therefore anticipated that ferric and magnesium hydroxides are indifferent to the catalytic action.

Each hydroxide, prepared by the interaction of the nitrate and aqueous ammonia, washed with a large quantity of water, and purified finally by electro-dialysis, was suspended in water and added to the acid earth. The decrease in the yield of the resinous matter just matches that caused by the dilution of the catalyst as in the case of silica gel.

It was also found that no resinous matter was produced by the use of a mixture of silica gel and ferric hydroxide ($\text{SiO}_2 : \text{Fe}_2\text{O}_3 = 3:4$) and, as already stated, Holmes's silica gel containing ferric hydroxide prepared from water glass and ferric chloride manifested almost no activity. From the above results, it may be safely granted that Fe_2O_3 and MgO are the simple diluents of the catalyst.

Thus, it appears that the rôles played by the chief constituents of Japanese acid earth in its catalytic action on naphthalene are fully explained and experimental results are in close agreement with the expectation. Water plays also an important part in the catalysis and its action will be discussed in details in another communication.

The Activities of Several Substances other than Japanese Acid Earth. Several other substances were analysed and examined on their catalytic activities on naphthalene by the same method. The data of experiments are shown in Table 4.

Table 4.

Substance	Locality of production	Chemical composition (%)								Yield of resinous matter (g.)
		Igni- tion loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Total	
Bentonite	Japan	7.22	63.30	20.30	3.00	1.12	0.54	3.38	98.89	0.25
Caoline	Japan	12.42	50.19	32.79	3.10	0.35	0	1.34	100.19	0.81
Clay I	Manchukuo	13.87	45.28	34.29	4.80 (+ TiO_2)	1.43	1.11	—	—	0.33
Clay II	Manchukuo	14.54	43.56	40.36	2.21 (+ TiO_2)	0.79	0.34	0.95	102.75	0.20
Diatom earth	Japan	5.10	80.70	11.90	3.90	0	0.20	0	101.80	0.22
Bauxite	India	12.87	1.22	74.78	10.35 (+ TiO_2)	0.49	0.16	—	—	0
Active charcoal	Germany	—	—	—	—	—	—	—	—	0

All the substance, which contain SiO_2 and Al_2O_3 as their chief constituents, possess more or less the catalytic activity on naphthalene.

According to Shigemune⁽⁸⁾, Japanese bentonite much resembles Japanese acid earth in its chemical composition, adsorptive powers for dyestuffs, and in many other respects, while Table 4 shows that its catalytic activity is only about one tenth of that of the acid earth. In the authors' opinion, its poor activity may be attributed to the comparatively large contents of CaO

(8) *Reports of Tokyo Imperial Industrial Research Laboratory*, **25** (1930), No. 10.

and K_2O , both the strong poisons to the catalysis, and therefore, if these poisons be removed, the activity may be raised. On treating the acid earth with hydrochloric acid, its composition as well as its catalytic activity suffers little change. In the case of bentonite, however, the ratio $CaO + K_2O/SiO_2$ is greatly diminished by the same treatment (in this respect there is a distinct difference between the two) and simultaneously its activity is raised enormously as shown in Table 5, exceeding even the greatest value of the acid earth given in Table 1. This result seems to be anticipated if the data given in Table 2 and 5 are compared, and bentonite is regarded as a species of the acid earth so far as the catalytic action is concerned.

Table 5.

Catalysts		$\frac{\text{Ig. loss}}{\text{SiO}_2} \times 100$	$\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} \times 100$	$\frac{\text{Fe}_2\text{O}_3}{\text{SiO}_2} \times 100$	$\frac{\text{CaO}}{\text{SiO}_2} \times 100$	$\frac{\text{MgO}}{\text{SiO}_2} \times 100$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2} \times 100$	Yield of resinous matter (g.)
Earth F	Before treatment with HCl	10.1	26.4	2.33	0.60	7.44	0.94	2.23
	After treatment with HCl	9.79	25.7	1.32	0.73	6.08	0.66	2.33
Bentonite	Before treatment with HCl	11.4	32.1	4.74	1.77	0.85	5.34	0.25
	After treatment with HCl	10.9	36.0	3.31	0.77	1.08	1.21	2.89

Further experiments were carried out to ascertain whether SiO_2 and Al_2O_3 could be replaced by TiO_2 and La_2O_3 respectively or not, and the combinations of $TiO_2-Al_2O_3$ and $SiO_2-La_2O_3$ were tested on the catalytic action. No resinous matter was found to be produced in both cases. Some interesting results might be attained if the above experiments be extended to various other metallic oxides.

Summary.

(1) Rôles played by the chief constituents of Japanese acid earth in its catalytic action on naphthalene have been studied. It has been found that the co-existence of SiO_2 and Al_2O_3 is essential to the catalysis and hydroxides of alkali and alkaline earth metals behave as poisons to the catalyst, while ferric and magnesium hydroxides are indifferent to the catalysis.

(2) Several substances other than Japanese acid earth, which contain SiO_2 and Al_2O_3 as their chief constituents, have been also examined on the same catalytic action.

(3) It has been tested whether TiO_2 and La_2O_3 can be substituted for SiO_2 and Al_2O_3 respectively in the catalytic action or not.

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THE SURFACE TENSIONS OF ETHYL ALCOHOL AND CARBON DISULPHIDE AT LOW TEMPERATURES.

By Tokuzo TONOMURA and Miss Kimi ISHIHARA.

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The surface tensions of some organic compounds were measured by the method of capillary rise by one of the present writers and were communicated in this Bulletin.⁽¹⁾ The present paper contains the results of the further measurements with ethyl alcohol and carbon disulphide. The details of the measurements were mentioned in the previous paper.⁽¹⁾

Ethyl alcohol and carbon disulphide used in the present measurements were the pure chemicals from Kahlbaum and purified in the usual ways. Their boiling points were 78.26°C. (759.5 mm.) and 46.00–46.10°C. (760.7mm.) respectively.

The experimental results are shown in Table 1 and 2 and diagrammatically in Fig. 1 and 2. The formula given at the bottom of each table has been obtained from the experimental data by the method of the least squares, and expresses the relation between temperature and surface energy, τ in the formula for carbon disulphide being the temperature measured from the critical temperature, 277.7°C.⁽²⁾ The formula for ethyl alcohol is quadratic and not of Eötvös type, for it is considered to have anomalous properties in several respects just like methyl alcohol dealt with in the previous paper. From these formulae the surface tensions at the corresponding temperatures have been calculated and are given in the sixth columns of the tables.

(1) Tonomura and Chujo, this Bulletin, **7** (1932), 259.

(2) Landolt-Börnstein's Tables, 5th ed. (1923), Vol. 1, 261.

Table 1.
The Surface Tension of Ethyl Alcohol.

Temp. °C.	Height cm.	Radius cm.	Density $D^{(4)}-d^{(3)}$	Surface Tension Dynes/cm.		Capillary
				σ (obs.)	σ (calc.)	
30.00	2.201	0.02498	0.7810	21.14	21.22	B
20.00	1.530	0.03692	0.7894	22.00	22.00	A
-12.16	2.523	0.02497	0.8166	25.30	25.19	B
-22.02	2.576	0.02498	0.8250	26.10	26.10	B
-31.49	1.789	0.03692	0.8332	27.15	27.04	A
-43.21	2.708	0.02498	0.8453	28.11	28.32	B
-52.83	2.786	0.02497	0.8517	29.12	29.27	B
-62.49	1.926	0.03692	0.8602	30.17	30.29	A
-69.75	2.905	0.02497	0.8667	30.90	31.06	B
-74.73	1.989	0.03692	0.8710	31.54	31.59	A
-80.52	2.995	0.02497	0.8762	32.21	32.22	B
-89.09	3.054	0.02497	0.8838	33.12	33.17	B
-93.03	2.083	0.03692	0.8874	33.64	33.61	A

$$\sigma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 703.09-1.3901T+0.0004318T^2$$

Table 2.
The Surface Tension of Carbon Disulphide.

Temp. °C.	Height cm.	Radius cm.	Density $D^{(3)}-d^{(3)}$	Surface Tension Dynes/cm.		Capillary
				σ (obs.)	σ (calc.)	
20.00	2.089	0.02497	1.2617	32.38	32.33	B
10.00	2.152	0.02497	1.2772	33.76	33.89	B
-1.85	1.510	0.03691	1.2939	35.66	35.75	A
-11.98	1.567	0.03691	1.3082	37.42	37.37	A
-14.43	1.576	0.03692	1.3117	37.69	37.76	A
-14.65	2.354	0.02497	1.3120	37.93	37.79	B

- (3) Landolt-Börnstein's Tables, 5th ed. (1923), Vol. 1, 271.
- (4) International Critical Tables, Vol. 3, 27.
- (5) Ibid., 23.
- (6) Landolt-Börnstein's Tables, 5th ed. (1923), 281.

Table 2. (Concluded)

Temp. °C.	Height cm.	Radius cm.	Density $D-d$	Surface Tension Dynes/cm.		Capillary
				σ (obs.)	σ (calc.)	
-21.29	1.613	0.03691	1.3214	38.85	38.87	A
-24.80	2.427	0.02497	1.3265	39.53	39.43	B
-29.93	2.467	0.02498	1.3338	40.42	40.27	B
-31.47	1.669	0.03691	1.3359	40.63	40.53	A
-41.80	2.539	0.02497	1.3506	42.10	42.22	B
-42.39	1.725	0.03691	1.3514	42.47	42.32	A

$$\sigma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 2.0007 (\tau - 9.28)$$

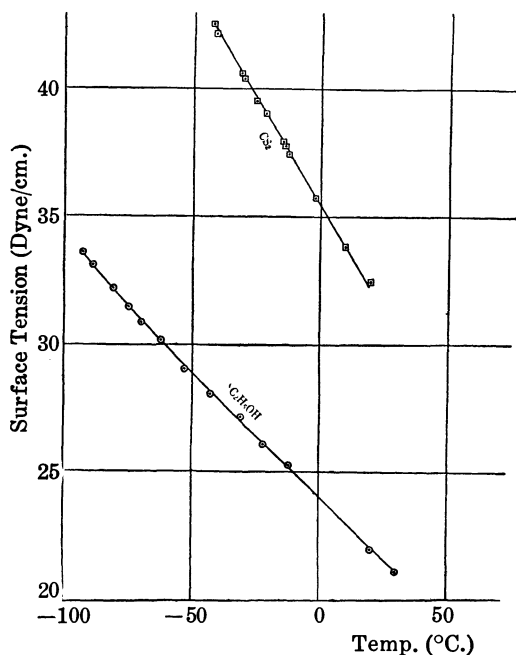


Fig. 1.

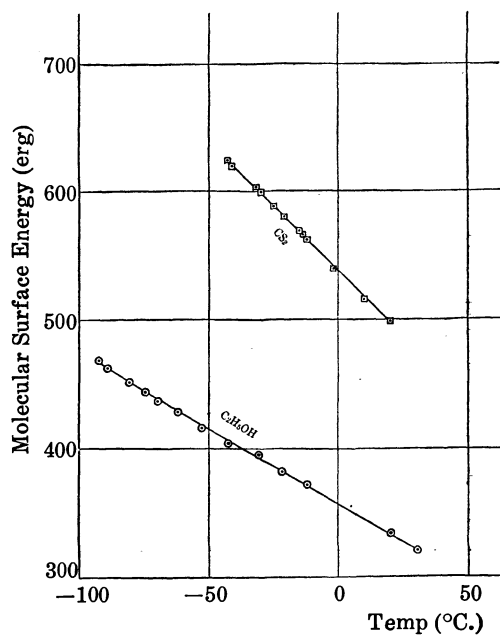


Fig. 2.

The writers wish to express their hearty thanks to Prof. S. Mitsukuri for his suggestion and guidance.

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THE CHEMICAL CHANGE OF CARBON DISULPHIDE UNDER ELECTRODELESS DISCHARGE.*

By Misao EMI.

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There have been many investigations to prepare carbon monosulphide,⁽¹⁾ among which the work by J. Dewar and H. O. Jones appears to be the most important. They decomposed the vapour of carbon disulphide at a low pressure of about 15 mm. under silent discharge in an ozonizer.

The present author decomposed the vapour of carbon disulphide under electrodeless discharge and examined the change. The vapour was passed through a discharge apparatus, and to attain a pressure sufficiently low to effect electrodeless discharge, a bulb containing carbon disulphide was connected with the reaction vessel by means of a long capillary tube with a diameter of about 0.1 mm., and the vapour coming out of the reaction vessel was condensed by cooling with liquid air, so that carbon disulphide distilled continuously through the reaction vessel. Further details of the apparatus are shown in Fig. 1.

Electrodeless discharge was effected by connecting two annular copper stripes on the reaction vessel to a supply of an alternating current of a frequency of approximately 10^7 cycles per second, which was generated from an alternating current of 200 cycles per second and about 2000–3000 volts by using a small transmitting valve. The circuit is shown diagrammatically in Fig. 2.

To purify carbon disulphide (from Hopkin and William Co., Ltd.), it was first distilled at about 46° , shaken with concentrated sulphuric acid, then with mercury, and finally with lime, and redistilled at 46° . When carbon disulphide (50 c.c.) was placed in bulb A and the bulb was cooled in ice, the

* Cf. J. J. Thomson, The Electrodeless Discharge through Gases, *Phil. Mag.*, Nov. 1927; J. S. Townsend and R. H. Donaldson, Electrodeless Discharge, *Phil. Mag.*, Jan. 1928; G. Mierdel, Untersuchungen über den Elektrodenlosen Ringstrom. *Ann. Physik*, Nr. 5, 1928; S. B. Bhatnager and Rama Krishna Sharma, Chemical Reaction under Electrodeless Discharge, *J. Indian Chem. Soc.*, June, 1928.

(1) M. Berthelot, *Ann. chim. phys.*, (3), **53** (1858), 142; A. W. Hofmann, *Ber.*, **3** (1870), 197; T. Sidot, *Compt. rend.*, **69** (1869), 1303; S. M. Losanitsch, *Ber.*, **30** (1897), 135; **40** (1907), 4656; J. Thomsen, *Z. anorg. Chem.*, **34** (1903), 187; A. Deninger, *J. prak. Chem.*, **51** (1895), 346; J. Dewar and H. O. Jones, *Proc. Roy. Soc., A*, **83** (1910), 408, 526; **85** (1911), 574. Further cf. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VI, p. 94.

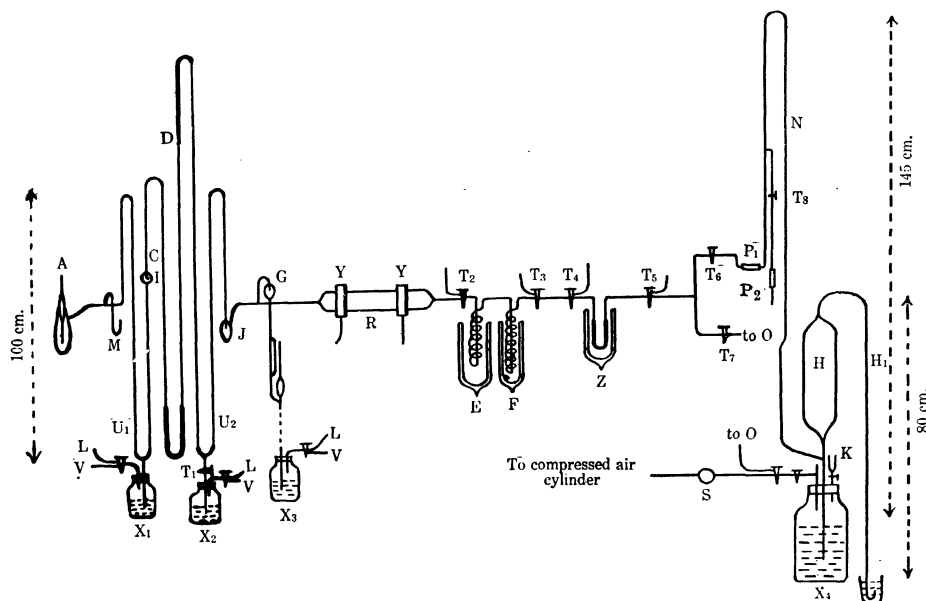


Fig. 1. A: bulb containing carbon disulphide. M: manometer. CD: capillary tube. I and J: traps for mercury. GX_3 : McLeod gauge. R: reaction vessel (about 250 c.c.). Y: annular copper stripes. E and F: condensers. Z: spare condenser. T_1 , T_2 , T_3 , T_4 , T_5 , T_6 , T_7 and T_8 : taps. Condensed carbon disulphide is removed from T_2 , T_3 , T_4 and T_5 . The vapour of carbon disulphide attacks tap grease, and hence it is necessary to grease the taps frequently to avoid leaks. HX_4 : Toepler pump to drive the gas from H into capillary tube H_1 . X_1 , X_2 , X_3 and X_4 : mercury reservoirs. K: funnel for supplying mercury to keep the mercury level of X_4 constant. S: safety valve. O: Cenco Hyvac pump. It is necessary to apply a pressure of about 600 mm., and tube N extends to about 145 cm. above the mercury level in X_4 . Compressed air is used to expel the gas from cylinder H, the pressure being controlled to about 0.8 atmosphere by safety valve S. U_1 and U_2 : long glass U-tubes for controlling the flow of the gas. L's: air is supplied by L's. The air is dried with $CaCl_2$, conc. H_2SO_4 , potash, and finally with P_2O_5 . V's: The air in the reservoirs is sucked from V's. Mercury goes up to the bottom of U_1 or U_2 and stop the flow of the gas when air is allowed from L, and goes down into the reservoir when air is sucked from V. P_1 and P_2 : tubes for drying the gas and the air flowing to Toepler pump respectively.

vapour pressure was found 128 mm. mercury, which was higher than the values obtained by H. V. Siemens (127 mm.) and by Henning and Stock (127.25 mm.).

To fill bulb A with carbon disulphide, the bulb was communicated with a Cenco Hyvac pump through a phosphorus pentoxide tube, evacuated, and dried, and liquid carbon disulphide was put in. After carbon disulphide having been frozen by cooling in liquid air, the bulb was evacuated through the phosphorus pentoxide tube as far as possible, and then sealed off.

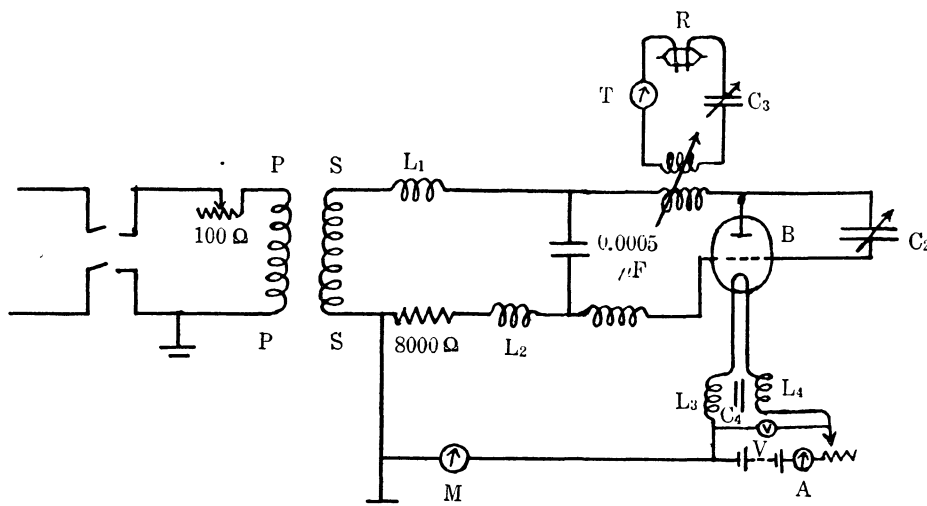


Fig. 2. L_1, L_2 : pyrex tubes of 2' 6'' length and $1\frac{1}{8}$ '' - $1\frac{1}{4}$ '' diameter, 2' being wound with D.S.C. copper wire of 32 S.W.G. L_3, L_4 : one pyrex tube of $1\frac{1}{2}$ '' diameter and 16'' length, wound doubly with D.C.C. copper wire of 16 S.W.G. C_4 : glass tube with copper foil on its inner wall to slide inside the tube of L_3 and L_4 . C_2, C_3 : variable condensers, each consisting of two copper sheets of $4'' \times 4'' \times \frac{1}{16}$ '' , mounted on pillars so that the space between them can be adjusted. M : milliammeter (0-30 m.a.). T : thermoammeter (0-12 amp.). B : Marconi valve (12.5 volts, 5.5 amp.). P : primary coil of the transformer. S : secondary coil of the transformer. R : reaction vessel. A : ammeter (0-10 amp.). V : voltmeter (0-15 volts).

$U_1, U_2, T_2, T_3, T_4, T_5$ and T_6 were then all communicated with the Toepler pump, and condenser E was placed in liquid air, and thus the vapour of carbon disulphide was allowed to flow from bulb A and to carry any residual air with it, the pump removing continuously the carried air. It took a long time (about two days) to expel air from the apparatus because of the slowness of the flow of the gas.

The vapour of carbon disulphide in the apparatus was tested on purity in the following manner. U_1 and U_2 were shut, condenser E previously evacuated as highly as possible was placed in liquid air, and taps T_2 and T_3 were then shut. The mercury in the McLeod guage was allowed to rise by adjusting the pressure in the mercury reservoir X_3 to the atmospheric pressure. U_1 and U_2 were then opened; in 5 minutes the mercury fell by 50 mm., and then U_1 was shut and T_2 opened. In about 10 minutes U_2 was shut and the pressure was read on the guage during about half an hour, and found constant at 0.005 mm. The initial pressure of the carbon disulphide in the

reaction vessel being 50 mm., the ratio of the pressure of air to that of carbon disulphide can not be greater than 0.005/50, that is 0.01 per cent.

The pressure of the vapour of carbon disulphide in the reaction vessel in the steady state was determined in the following manner. The whole apparatus was evacuated to about 0.005 mm., and the vapour of carbon disulphide was allowed to flow from bulb A cooled in ice (the vapour pressure being 128 mm. here) into the apparatus. Condenser E was then cooled in liquid air and the pressure was read, Table 1.

Table 1.

Time (min.)	Pressure (mm.)
0	0.08
5	„
10	„
15	„
20	„
25	„
35	„

Table 2.

Time (min.)	Pressure (mm.)	Time (min.)	Pressure (mm.)	Time (min.)	Pressure (mm.)
0	0.085	30	0.0925	60	0.075
4	„	35	„	65	„
9	„	40	„	72	„
15	0.0925	45	„	80	„
20	„	50	0.075	88	„
25	„	55	„	90	„

When the pressure in the apparatus was steady (0.08 mm.), condenser F as well as E was cooled in liquid air, and the vapour of carbon disulphide was subjected to the action of electrodeless discharge. The pressure was read continually, Table 2. The pressure fell to 0.075 mm. in fifty minutes and stayed steady there.

When electrodeless discharge was stopped, the whole wall of the reaction vessel was found to be covered with brown solid, and the narrow necks with dark solid. On removing liquid air from condenser E, instantaneous detonation took place with a flash, and the upper part of the condenser was covered with a dark lustrous solid mass, and the bottom with a dark brown powder, while no liquid was found.

A part of the deposit on the wall of the reaction vessel was dissolved in carbon disulphide, when a brown solution resulted. On adding a drop of concentrated sulphuric acid to this solution, a brown precipitate was formed. The deposit on the bottom of condenser E was dissolved in carbon disulphide to a purplish brown solution, which gave a purple precipitate on adding a drop of concentrated sulphuric acid. These solid substances appear to be the polymers of gaseous carbon monosulphide in different degrees of polymerization.

The black lustrous substance on the wall of the reaction vessel may probably be a polymer of carbon ditritia-sulphide $(C_3S_2)_x$ which might be formed together with the polymers of monosulphide. It seems that mercury also deposited on the wall of the condenser.

It can not be said that carbon monosulphide CS existed as a stable gas. It is very interesting that Dewar and Jones, too, reported the formation of a brown mass accompanied by a flash and detonation. More precise and quantitative investigation will further be made.

In conclusion the author wishes to express his hearty thanks to Prof. F. G. Donnan of the University College, London, where this investigation was made by virtue of his kind suggestion and encouragement, and to acknowledge the kind advice and great help rendered by Dr. R. W. Lunt during the course of the experiments.

RELATION BETWEEN THE TEMPERATURE AND THE pH
VALUE OF THE BOTTOM DEPOSITS FROM
POND TAKASUKANUMA.

By Ken SUGAWARA.

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Knowledge of the relation between the temperature and the pH value of lake deposits is important to biological and biochemical studies of them. If a sample of deposits manifests different pH values at different temperatures, such will naturally have different pH values also in the bottom of the lake as the temperature varies along with the seasons. Such a variation of pH may, on one hand, have seasonal influence on the benthic fauna and flora, and, on the other, it may affect the chemical changes taking place in the bottom.

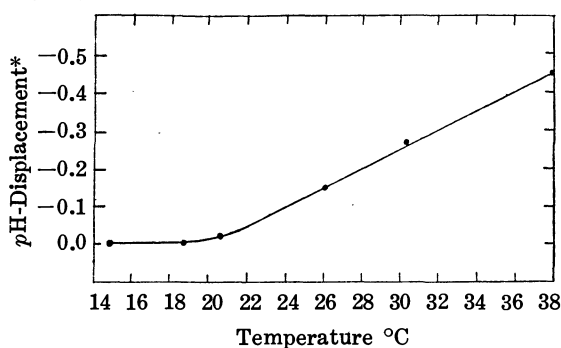
Now, the measurement of the pH value of bottom deposits is practically made in the laboratory instead of on the spot. Then, it happens very often that the temperature of the laboratory differs from that of the spot, and the observed values must be corrected in order to obtain the real values.

When the author made the investigation of the annual variation of the pH value in the deposits of Pond Takasukanuma in the course of the years

1932 to 1933, in parallel with studies on other factors affecting deposit metabolism,⁽¹⁾ it was necessary to establish the relation between the temperature and the pH value.

Displacements of the pH value between two temperatures were measured in five experiments. The results are shown in the table, by aid of which a curve of temperature-pH-displacement was drawn. This curve serves to compute the pH value of the actual place from that observed in the laboratory. Thus, on the 9th of August, 1933, the temperature was read 31.0°C. in laboratory and 14.9°C. in the bottom of the lake, and the observed value pH 6.46 is reduced to 6.73 by correction of +0.27.

	Temp. °C.	pH	pH-displacement
I	15.4	6.68	0.01
	19.8	6.67	
II	14.8	6.16	0.02
	20.7	6.14	
III	18.8	6.48	0.15
	26.0	6.33	
IV	18.8	6.52	0.26
	30.5	6.26	
V	19.1	6.83	0.45
	38.0	6.38	



* Referring to the pH value of the horizontal part of the curve below about 18.7°C.

It is remarkable that the curve runs horizontally below 18.7°C., and that the horizontal part seems to extend further as the curve runs below 14.8°C., the lowest temperature of the experiments. This leads to the supposition that the bottom deposits are so conditioned, at least in the particular case of the deepest part of Pond Takasukanuma, that the pH value remains constant, so far as the dissociation equilibrium in it is concerned, because the temperature of that part of the bottom does not exceed 17.5°C. throughout the whole year, as stated in the report cited.

It is of question whether these relations obtained can be applied in general to any type of lakes and to any part of their bottoms. In fact, even in Takasukanuma, the bottom is warmed to a higher temperature in its shallower part, and it is highly possible that pH varies with the seasons solely owing to dissociation equilibrium.

Studies will be continued further along these lines.

(1) *Japanese Journal of Limnology*, Vol. IV. No. 4.

Experimental.

Thoroughly kneaded sample (1 c.c.) is well stirred with 2 c.c. of distilled water for one minute, then a knife-tipful of quinhydrone is added and the mixture is stirred further for half a minute. A platinum electrode is inserted and *pH* is measured in 3 minutes potentiometrically referring to the saturated calomel half cell.

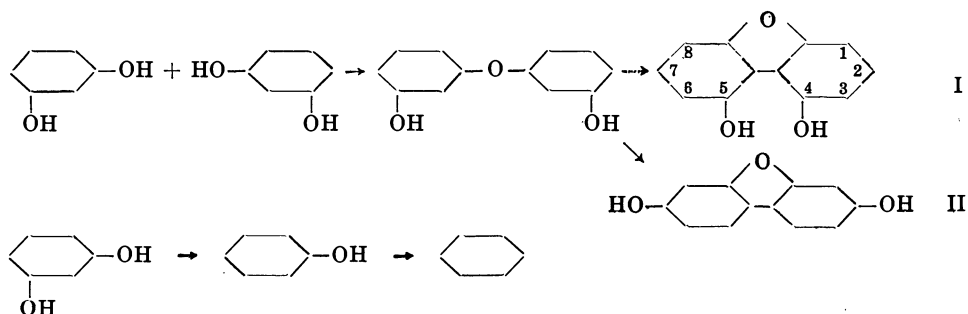
Chemical Laboratory, Tokyo High School.

THE CONSTITUTION OF THE HYDROXY-DERIVATIVES OF DIPHENYLENE OXIDE OBTAINED FROM RESORCINOL.

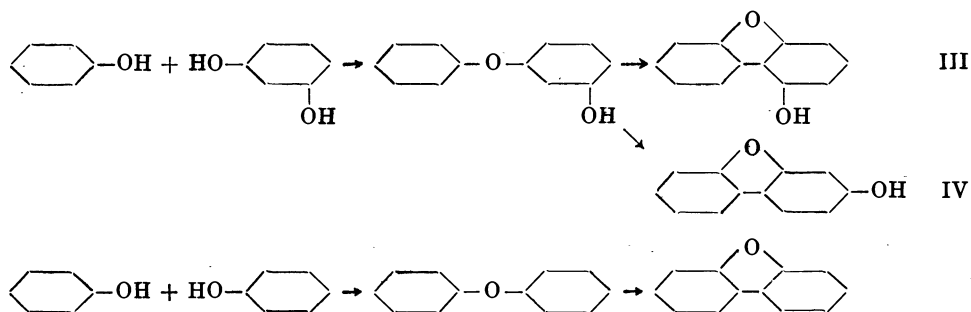
By Kiyoharu TATEMATSU and Bennosuke KUBOTA.

Received August 27th, 1934. Published October 28th, 1934.

It was previously reported⁽¹⁾ that resorcinol undergoes a certain reduction and condensation under the influence of the blue oxide of tungsten at 500–550°, and gives two substances besides benzene, phenol, and diphenylene oxide. Of the two substances, one melting at 138–138.5° was assumed by Y. Tsuzuki to be 4-hydroxydiphenylene oxide (III) from the observation of its decomposition product as well as of absorption spectra, and the other melting at 241–242° was considered 4,5-dihydroxydiphenylene oxide (I). The process of the reactions giving these two compounds appeared to be represented by the dotted arrows in the scheme shown below :



(1) B. Kubota, Y. Fujimura, and K. Akashi, *Scientif. Pap. Inst. Phys. Chem. Research, Japan*, **2** (1925), 185; Y. Tsuzuki, *ibid.*, **6** (1927), 301.



With the view of ascertaining the constitutions of these compounds the monohydroxydiphenylene oxide melting at 138–138.5° was again examined. It was compared with 2-hydroxydiphenylene oxide obtained by us from Cullinane's 2-aminodiphenylene oxide⁽²⁾ by means of the diazo-reaction. The acetyl-, methyl-, and dinitro-derivatives of them were also compared. As shown in Table 1, the melting points of the monohydroxydiphenylene oxide from resorcinol and its derivatives are in good agreement with those of the corresponding compounds obtained from 2-aminodiphenylene oxide, and moreover, the mixed melting point of the two monohydroxydiphenylene oxides gave no depression.

Table 1. Comparison of the Melting Points.

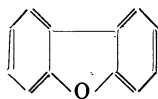
Substance	From resorcinol	From 2-amino-diphenylene oxide
Hydroxydiphenylene oxide	138–138.5°	138–138.5°
Acetyl-derivative	111–111.5°	111–111.5°
Methyl-derivative	93–94°	97–97.5°
Dinitro-derivative	216–217° (decomp.)	216.5–217° (decomp.)

These facts indicate evidently that the compound in question obtained from resorcinol is none other than 2-hydroxydiphenylene oxide (IV), and may naturally suggest that the other substance obtained from resorcinol, melting at 241–242°, is more probably 2,7-dihydroxydiphenylene oxide (II). Although the latter problem is yet under investigation, the main processes of the reactions may be represented by the real arrows in the scheme shown above.

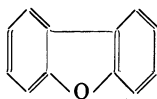
(2) N. M. Cullinane, *J. Chem. Soc.*, **1930**, 2267.

The comparative study of the absorption spectra was the chief ground of the previous arguments concerning the constitutions of these substances. As the previous authors pointed out, the absorption curve of 2-hydroxydiphenylene oxide has a striking resemblance in the form to that of *o*-hydroxydiphenyl but not to that of *p*-hydroxydiphenyl. But it is remarkable that this curve resembles that of 2,4-dihydroxydiphenyl and especially that of diphenylene oxide. As seen from the curves given in the experimental part, the influence of the hydroxyl-group on the absorption spectra is different with the position of the group in the diphenyl ring and also in the diphenylene oxide ring. Thus, if a hydroxyl-group is introduced to diphenyl in the ortho-position with respect to the diphenyl linkage, the absorption spectra are strongly influenced, while the effect of a para-hydroxyl-group is so weak that the form of the curve is hardly affected. From these points of view formula IV is highly probable for the monohydroxydiphenylene oxide melting at 138–138.5°.

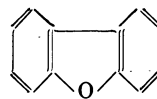
Further the constitution of this compound was confirmed by studying its bromination product. Applying Kekulé's formula to the two benzene rings in diphenylene oxide, three formulae (1), (2), and (3), which are conditioned by the two possible arrangements of bonds in each benzene ring, may be considered :



(1)



(2)

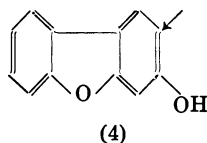


(3)

Two of them, (2) and (3), possessing respectively one and two double bonds common to the benzene and the furan rings should be under greater intramolecular strain, because two and four β intravalency angles are respectively included in the furan rings of them, and, therefore, according to Mills's hypothesis,⁽³⁾ considerable distortion of the natural valency directions should be required to approximate these angles to the intravalency angle of the furan ring. In formula (1) in which single bonds only are common to the benzene and the furan rings, four α intravalency angles are brought into the furan ring, and as the α -angle does not differ from the intravalency angle of the furan ring so much as the β -angle does, the molecule of the form (1) should suffer less strain. Thus Mills's hypothesis indicates that the form (1) is the most stable constitution of diphenylene oxide. If our consideration is correct, the most stable form of 2-hydroxy-

(3) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, **1930**, 2510.

diphenylene oxide must be (4), and the substitution of bromine should take place mainly at the 3-position as indicated by the arrow :



We examined accordingly the action of bromine on 2-hydroxydiphenylene oxide, and as expected, the main product was 3-bromo-2-hydroxydiphenylene oxide. The orientation of the bromine atom in the bromo-2-hydroxydiphenylene oxide was established as follows :

The bromo-2-aminodiphenylene oxide, which was obtained by bromination and subsequent hydrolysis of the 2-acetamino-compound prepared from Cullinane's 2-nitrodiphenylene oxide,⁽⁴⁾ was changed into the corresponding bromo-2-hydroxydiphenylene oxide by the diazo-reaction, which was found identical with the bromination product of 2-hydroxydiphenylene oxide. On replacing the amino-group by hydrogen, the bromo-2-aminodiphenylene oxide gave 3-bromodiphenylene oxide of F. Mayer and W. Krieger.⁽⁵⁾ Hence, the position of the bromine atom in the bromo-2-hydroxydiphenylene oxide is either 3 or 6.

2-Acetaminodiphenylene oxide, obtained by acetylation of the 2-amino-compound, gave a nitro-2-aminodiphenylene oxide on nitration and subsequent hydrolysis. This nitro-amino-compound was reduced to a diamino-compound, which proved to be an *o*-diamine, because it combined with benzil and phenanthrene-quinone to close a quinoxaline ring.⁽⁶⁾ Hence, the position of the nitro-group must be either 1 or 3.

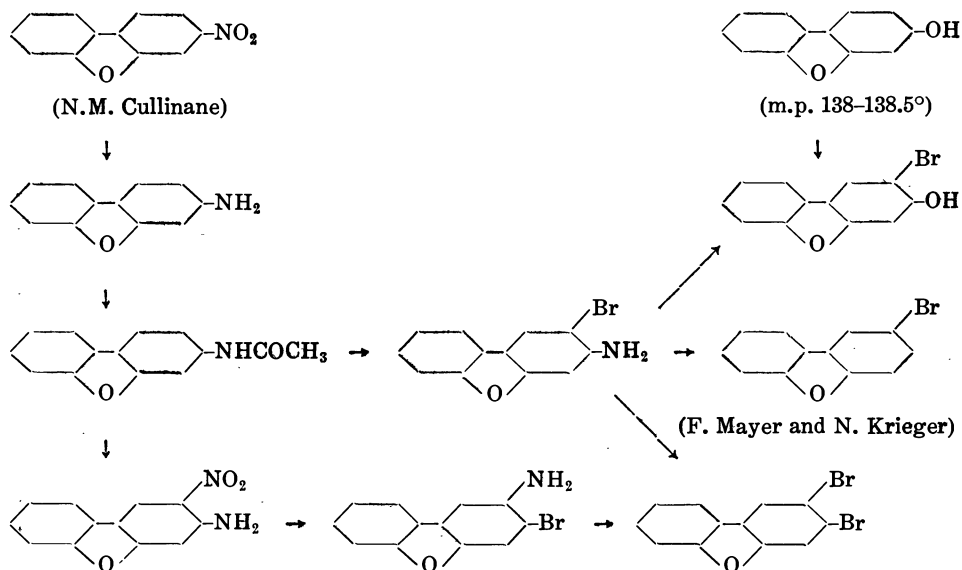
On replacing the amino-group by bromine and subsequently reducing the nitro-group, the nitro-2-aminodiphenylene oxide was converted into an amino-2-bromodiphenylene oxide. From this amino-2-bromodiphenylene oxide and from the bromo-2-aminodiphenylene oxide mentioned above, Sandmeyer's reaction yielded the same dibromo-compound. Hence the nitro-group in the above-mentioned nitro-2-aminodiphenylene oxide and the bromine atom in the bromo-2-aminodiphenylene oxide, and consequently the bromine atom in the bromo-2-hydroxydiphenylene oxide, must be in the same position, and that in 3. Thus it was established that the main product of bromination of 2-hydroxydiphenylene oxide is 3-bromo-2-hydroxydiphenylene oxide.

(4) N. M. Cullinane, loc. cit.

(5) *Ber.*, **55** (1922), 1659.

(6) W. Borsche and B. Schacke, *Ber.*, **56** (1923), 2498.

The above-mentioned nitro-2-aminodiphenylene oxide melting at 222° was supposed by Cullinane⁽⁷⁾ to possess the nitro-group in the 1-position, but it was thus established that the nitro-group is in the 3-position.



Experimental.

(1) **2-Hydroxydiphenylene oxide.** 2-Nitro-diphenylene oxide is the main product of nitration of diphenylene oxide.⁽⁸⁾ It was converted into 2-aminodiphenylene oxide by reducing with stannous chloride in glacial acetic acid saturated with hydrogen chloride. The product crystallized readily from dilute alcohol in colourless needles, m.p. $99-99.5^{\circ}$ (W. Borsche and W. Bothe give 94°).

The sulphate of the 2-amino-compound, obtained by heating 2-amino-diphenylene oxide (12 g.) in 5% sulphuric acid (330 c.c.), was diazotized at 0° with sodium nitrite (4.5 g.) in water (12 c.c.), when the diazo-compound gradually separated out in brown yellow needles. After being allowed to stand over night at 0° , the product was gradually put into a boiling 50% copper sulphate solution (400 g.),⁽⁹⁾ and the mixture was boiled in a flask with a reflux condenser for two hours. The diazo-compound which was

(7) N. M. Cullinane, loc. cit.

(8) W. Borsche and W. Bothe, *Ber.*, **41** (1908), 1940.

(9) D. R. P., 167211.

formerly said to be stable,⁽¹⁰⁾ was thus decomposed, and the hydroxy-compound separated out in lustrous crystals. It was recrystallized from dilute alcohol, when it separated out in colourless plates melting at 138–138.5° (Yield 5 g.).

On adding a drop of ferric chloride solution to a solution of the substance, made by dissolving it in a very small quantity of alcohol and then adding water till the solution just began to become turbid, it gave a yellowish green colour, which turned light brown on addition of a dilute soda solution.

The acetyl-derivative, obtained by heating the hydroxy-compound with acetyl chloride, crystallized from concentrated acetic acid in large prisms melting at 111–111.5°.

The monomethyl-derivative, obtained by treating the hydroxy-compound with dimethyl sulphate and caustic soda solution, crystallized from dilute alcohol in plates, m.p. 97–97.5°. It melts somewhat higher than the methyl-derivative of the monohydroxydiphenylene oxide from resorcinol (93–94°).

The dinitro-derivative, obtained by nitration of the hydroxydiphenylene oxide in glacial acetic acid with concentrated nitric acid, crystallized from glacial acetic acid in small yellow prisms melting at 216–217° (decomp.).

These properties of the 2-hydroxydiphenylene oxide are in good agreement with those of the hydroxydiphenylene oxide described by the previous authors.⁽¹¹⁾ Moreover, the mixed melting of the two substances gave no depression, indicating the identity of the two substances.

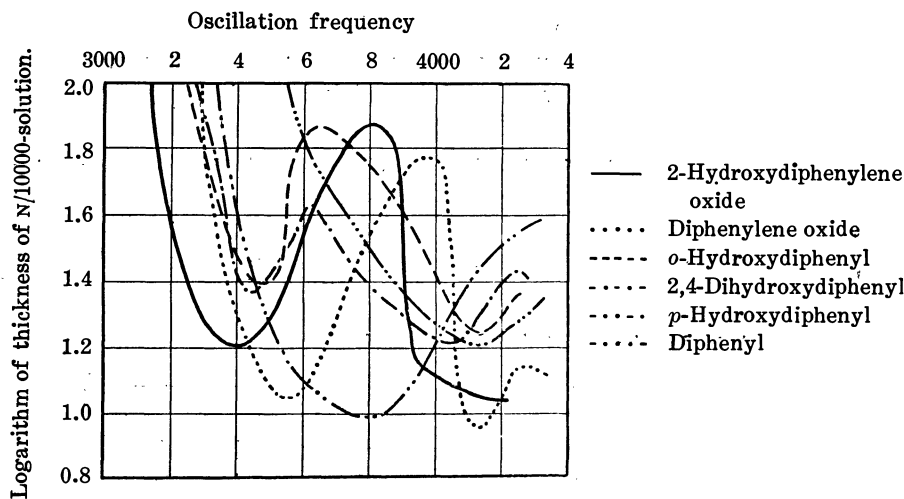
The absorption curves. The results of a comparative study on the absorption curves of hydroxydiphenylene oxide from resorcinol, its acetyl-derivative, diphenylene oxide, mono- and di-hydroxydiphenyls are shown in the figure. All observations of absorption spectra were made in alcoholic solution.

The curves of the 2-hydroxydiphenylene oxide from the 2-nitro-compound and its acetyl-derivative have not been drawn, for they coincide with the curves of the hydroxydiphenylene oxide from resorcinol and diphenylene oxide respectively.

As already pointed out, the form of the curve of the hydroxy-compound probably depends chiefly upon the diphenylene oxide ring, and the position of the hydroxyl-group is not to be decidedly determined by this result only.

(10) W. Borsche and W. Bothe, loc. cit.

(11) B. Kubota, Y. Fujimura, and K. Akashi, loc. cit.; Y. Tsuzuki, loc. cit.



(2) **3-Bromo-2-hydroxydiphenylene oxide from 2-hydroxydiphenylene oxide.** Bromine (0.5 g.) dissolved in glacial acetic acid (1 c.c.) was added drop by drop at 0° to a solution of 2-hydroxydiphenylene oxide (0.6 g.) in the same solvent, and two hours later a large quantity of water was poured, when a white crystalline precipitate was formed. It was recrystallized from dilute acetone, colourless needles melting at 113° – 113.5° (Yield 0.65 g., 70% of the theoretical). Treated with dimethyl sulphate and a caustic soda solution, this compound gave a methyl-derivative melting at 147 – 148° .

(3) **3-Bromo-2-hydroxydiphenylene oxide from 2-acetaminodiphenylene oxide.** (i) *2-Acetaminodiphenylene oxide.* 2-Nitrodiphenylene oxide was reduced to 2-aminodiphenylene oxide by the action of stannous chloride in acetic acid saturated with hydrogen chloride. The amino-compound (3 g.) was dissolved in absolute alcohol (30 g.) and to this solution acetic anhydride (15 g.) was added. After being kept for half an hour at ordinary temperature, the solvent was evaporated on the water bath. The operation of adding alcohol and evaporating was repeated until a white crystalline mass was obtained. It was recrystallized from dilute alcohol, colourless flat needles melting at 176.5 – 177° (Yield 3 g.).

(ii) *3-Bromo-2-acetaminodiphenylene oxide.* 2-Acetaminodiphenylene oxide (0.8 g.) was dissolved in glacial acetic acid (15 c.c.) and bromine (0.6 g.) in the same solvent (1.5 c.c.) was added at room temperature, when the colour of bromine soon disappeared and a white crystalline precipitate separated out. After an hour, a sufficient quantity of water (30 c.c.) was added. The crystalline precipitate was collected and well washed with

dilute acetic acid. It was recrystallized from dilute acetone, colourless needles, m.p. 195–195.5°. (Yield 0.8 g., 70% of the theoretical. Found: N, 4.56. Calc. for $C_{14}H_{10}O_2NBr$: N, 4.60%.)

(iii) *3-Bromo-2-aminodiphenylene oxide*. 3-Bromo-2-acetaminodiphenylene oxide was boiled with alcoholic potash (2%, 50 c.c.) for one hour, and sufficient water (100 c.c.) was added to the solution, when a white crystalline precipitate was formed. It was recrystallized from dilute alcohol, colourless plates, m.p. 129–130°. (Yield almost theoretical. Found: N, 5.30. Calc. for $C_{12}H_8ONBr$: N, 5.34%.)

(iv) *3-Bromo-2-hydroxydiphenylene oxide*. 3-Bromo-2-aminodiphenylene oxide (0.15 g.) was heated in 10% sulphuric acid (15 c.c.) to obtain its sulphate. The sulphate was diazotized with sodium nitrite (0.05 g.) at 0°. On keeping the reaction mixture over night at 0°, the diazo-compound separated in a yellow crystalline precipitate. It was dissolved in a minimum quantity of water and the solution was added to a 50% solution of copper sulphate (40 g.), the latter being distilled during the addition so as to keep the concentration of copper sulphate constant.⁽¹²⁾ After all the diazotized solution was added, the distillation was continued under the addition of water until no more crystals distilled. The crystalline substance was recrystallized from dilute alcohol, colourless needles melting at 113–113.5°. No depression was observed in the mixed melting point of this substance and the bromo-2-hydroxydiphenylene oxide obtained by the direct bromination of 2-hydroxydiphenylene oxide.⁽²⁾

(4) *3-Bromodiphenylene oxide*. 3-Bromo-2-aminodiphenylene oxide (0.1 g.) was converted into its hydrochloride by heating with 10% hydrochloric acid (15 c.c.). The hydrochloride was diazotized with sodium nitrite (0.035 g.). After three hours, this solution was made alkaline with caustic soda solution, filtered from reddish brown precipitate, and poured into sodium stannite solution made from stannous chloride (0.1 g.) and an excess of caustic soda solution. Nitrogen was evolved and a white crystalline precipitate separated. After being allowed to stand over night at room temperature, the precipitate was collected and recrystallized from dilute alcohol. It crystallized in colourless plates melting at 107–108°, and gave no depression of the melting point when mixed with 3-bromodiphenylene oxide prepared from diphenylene oxide by direct bromination in carbon disulphide.⁽¹³⁾

(5) *2,3-Dibromodiphenylene oxide from 3-bromo-2-aminodiphenylene oxide*. 3-Bromo-2-aminodiphenylene oxide (0.15 g.) was heated in hy-

(12) D. R. P., 167211.

(13) F. Mayer and W. Krieger, loc. cit.

drobromic acid (1.5 c.c. of an acid with density 1.38 diluted to 10 c.c.). The hydrobromide thus obtained was diazotized at 0° with sodium nitrite solution. After being kept over night at 0°, it was filtered from some reddish brown precipitate and was poured into cuprous bromide solution (0.2 g. cuprous bromide dissolved in 4 c.c. of hydrobromic acid with density 1.38 and diluted to 10 c.c.), when nitrogen was evolved and some yellow precipitate was obtained. It was recrystallized from 50% alcohol, when it separated out in plates melting at 150–150.5° (Yield 0.02 g.).

(6) **2,3-Dibromodiphenylene oxide from 3-nitro-2-aminodiphenylene oxide.** 3-Nitro-2-aminodiphenylene oxide was obtained from 2-acetaminodiphenylene oxide in a manner just as described by the previous authors.⁽¹⁴⁾

(i) *3-Nitro-2-bromodiphenylene oxide.* As the basicity of 3-nitro-2-aminodiphenylene oxide is extremely weak and neither its sulphate nor its hydrochloride is stable in water, the diazotation of this compound was carried out by a special method.⁽¹⁵⁾ Sodium nitrite (0.026 g.) was dissolved in well cooled concentrated sulphuric acid (18 c.c.) and to it fine powder of 3-nitro-2-aminodiphenylene oxide was added at 0°. A small quantity of ice (8 g.) was added bit by bit into this solution and after being kept at 0° for one hour, it was poured on ice (70 g.). This diazo-solution was added to a solution of cuprous bromide in hydrobromic acid (1 g. of cuprous bromide dissolved in 18 c.c. of hydrobromic acid with density 1.38 and diluted to 50 c.c. with water), when nitrogen was evolved and a yellow crystalline precipitate separated out. After being allowed to stand over night, it was collected and recrystallized from alcohol, yellow needles melting at 171–172°. (Yield 0.4 g. Found: N, 5.05. Calc. for $C_{12}H_6O_3NBr$: N, 4.79%.)

(ii) *3-Amino-2-bromodiphenylene oxide.* 3-Nitro-2-bromodiphenylene oxide (0.38 g.) was dissolved in a solution of stannous chloride in glacial acetic acid saturated with hydrogen chloride, and after being allowed to stand over night at room temperature, this solution was heated on a water bath for half an hour. By adding an excess of caustic soda solution, the amino-compound was obtained in fine crystals. It was purified by recrystallization from dilute alcohol when it separated out in colourless needles melting at 172–172.5°. (Yield 0.2 g. Found: N, 5.43. Calc. for $C_{12}H_8ONBr$: N, 5.34%.)

(iii) *2,3-Dibromodiphenylene oxide.* 3-Amino-2-bromodiphenylene oxide (0.15 g.) was converted into its sulphate by heating with 10% sulphuric acid (30 c.c.) and the sulphate solution was diazotized with sodium nitrite (0.05 g.). After being allowed to stand over night, the diazo-solution was

(14) W. Borsche and B. Schacke, loc. cit.

(15) E. Misslin, *Helvetica Chim. Acta*, **3** (1910), 626.

filtered from reddish brown precipitate and poured into a solution of cuprous bromide in hydrobromic acid (0.2 g. of cuprous bromide dissolved in 5 c.c. of hydrobromic acid with density 1.38 and diluted to 15 c.c. with water), when nitrogen was evolved and an orange yellow precipitate separated out. After two hours this was collected and recrystallized from dilute alcohol, colourless plates, m.p. 150.5–151°. No depression was observed in the mixed melting point of this substance and 2,3-dibromodiphenylene oxide obtained from 3-bromo-2-aminodiphenylene oxide (5).

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THE CONCENTRATION OF DEUTERIUM IN SOME INDUSTRIAL WATERS.

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As the water from commercial electrolytic cells containing a little more deuterium than ordinary water is regarded as a convenient material for the preparation of heavy water, it seems worth while to examine the waters of other industrial sources on their deuterium contents. Thus, Newell and Ficklen⁽¹⁾ found that the water from some commercial chromium plating baths which had been operated for less than three years was heavier than ordinary water by 20 to 640 parts per million (p.p.m.); Washburn and Smith⁽²⁾ also examined the same sort of water but found that the excess in density was only 2 to 5 p.p.m.; Uhlmann⁽³⁾ called attention to the fact that the water from some laboratory storage batteries after six to ten years use was heavier than normal water by 33 p.p.m., suggesting that this water can be used as a starting material for the preparation of heavy water.

The present authors have also investigated some of the industrial waters on their deuterium contents by comparing their densities with that of normal water. The results are shown in the Table.

(1) L. L. Newell and J. B. Ficklen, *J. Am. Chem. Soc.*, **55** (1933), 2167.

(2) E. W. Washburn and E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305.

(3) W. Uhlmann, *Naturwissenschaften*, **22** (1934), 119.

Source of sample.	Period of operation	Readings in bouyancy balance.	Excess in density in p.p.m.	H ² : H ¹
(1) Commercial electrolytic cell	1 year	0.39°±0.00	28	1 : 2100
(2) Chromium plating bath	4 years	0.12°±0.00	7	1 : 3800
(3) Lead accumulator A.	9 years	0.01°±0.01	3	1 : 4400
" " B.	" "	0.00°±0.01	0	1 : 5000
" " C.	" "	0.00°±0.02	0	1 : 5000
(4) Edison battery A.	9 months	0.41°±0.02	28	1 : 2100
" " B.	6 months	0.38°±0.02	27	1 : 2100

The first sample to be investigated was the water from a commercial electrolytic cell, which, having been in use for all the year round, had been supplied with water sixty times its volume mainly owing to evaporation. The second sample was obtained from a commercial chromium plating bath running for nearly four years. During the process of plating, the evolution of hydrogen was hardly avoidable. The third samples were obtained from three different lead accumulators, all of which, having run for nearly nine years, had a supply of considerable amounts of water for the loss of the contents. The fourth samples were obtained from two Edison batteries, one being in use for about nine months in a part of coal mines, and the other for six months in another part of coal mines.

Various samples of water thus obtained were purified by the following processes: The water was filtered and distilled, after being neutralized if necessary, to free it from any dissolved substances; it was again distilled after being boiled with potassium permanganate in alkaline solution for nearly eight hours; then the distillate was redistilled twice, once with a few drops of sulphuric acid and once with some solid baryta. The water thus obtained was further subjected to three more successive distillations in the stream of air free from carbon dioxide, the first distillation being carried out under the addition of potassium permanganate and a few drops of sulphuric acid, the second under the addition of some solid baryta, and the final with a quartz condenser. The purity of the final distillate was determined by the conductivity method.

The density of the purified sample was determined referring to that of the ordinary water purified in the same way as above by the method of bouyancy balance using a quartz sinker. In order to increase the sensitivity of the balance, temperature a little lower than that of the room was employ-

ed, namely between 8° and 9°C., except the case (3) A, where the bath temperature was 23.80°C. The third column of the table shows the readings in the bouyancy balance in terms of degree, each being the mean of two independent determinations, except the case (3) A, where the mean of three independent determinations was taken.

If it is assumed that the increase in density is solely due to the enrichment of deuterium, the water from the commercial electrolytic cell contains about twice as much deuterium as ordinary water, which is almost the same for the cells which have been used for a longer period.⁽⁴⁾ Therefore, the water in the electrolytic cell seems to be capable of being concentrated up to this value, after which the rate of concentration becomes much slower. The present result for the chromium plating bath agrees fairly well with that of Washburn and Smith, but not with that of Newell and Ficklen. The result for the lead accumulators is found to be not in agreement with that of Uhlmann who found as much increase in density as 32 p.p.m. The degree of concentration for this case may be largely affected by the process of charging, as the evolution of hydrogen gas during this process can be regarded as the main cause of concentration. It seems rather plausible that our result for the lead accumulators is related in some way to the relatively poor separation efficiency obtained when dilute sulphuric acid solution is electrolysed between lead electrodes.⁽⁵⁾

The result for the Edison batteries is quite unexpected. The samples were taken from quite different sources and they were purified in the same way as the other samples. We are not yet sure whether the increase in density is really due to the concentration of deuterium or to some unseparable impurities included originally. We are still in the course of re-investigation of this case.

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(4) D. H. Rank, *J. Chem. Phys.*, **1** (1933), 750.

(5) T. Titani, K. Kurano, and M. Harada, this Bulletin, **9** (1934), 269.

ON THE CONTENT OF DEUTERIUM IN THE WATER OF CRYSTALLIZATION.

By K. OKABE, M. HARADA, and T. TITANI.

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It has been reported by Güntherschulze and Keller⁽¹⁾ that no concentration of deuterium occurs when the volume of a given amount of water is contracted by repeating the process of dissolving and crystallizing Na_2SO_4 in it. We have also examined the same process. Although the result has been negative, it may be worth while to state our method in some details, since it has been found by several investigators that the water crystallized in some native minerals was heavier than normal water.^{(2) (3)}

About 20 liters of tap water was saturated with Na_2SO_4 by dissolving the anhydrous salt in it. The solution was then quickly cooled down by dipping the containers in ice water. The deca-hydrate which crystallized out, after being separated from the mother liquor (R_1), was heated in a beaker to convert it into anhydrous salt, and the remaining clear solution (C_1) was then filtered. Both C_1 and R_1 , equal in volume, were subjected to the same process as mentioned above. A part of water (C_2) crystallized out from C_1 and the residual water (R_2) from R_1 were subjected to the third process, all the other water being discarded. The same process was repeated eight times until we obtained finally about 100 c.c. of water of crystallization and about an equal amount of residual water. The densities of these two parts of water, after being carefully purified, were compared with that of normal water by a quartz bouyancy balance. Both were found heavier than normal water by 2 parts per million, but no difference in density between themselves was found within one part per million, showing that no concentration occurred in this process. The same process carried out with Na_2CO_3 by Mr. Gotoh in our laboratory brought about the same result.

We may draw a conclusion that no isotopic fractionation occurs by the crystallization of water with such salts as above at least at low concentrations of deuterium and that the concentration of deuterium which were found in some of the native minerals might be due to the crystallizing out

(1) A. Güntherschulze and F. Keller, *Z. Elektrochem.*, **40** (1934), 182.

(2) E. W. Washburn and E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305.

(3) Peters, *Z. Elektrochem.*, **40** (1934), 474.

of the water that had been already concentrated in some way, presumably by a slow evaporation in a closed basin, as already pointed out by Washburn and Smith.⁽²⁾

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THE COLLOIDAL BEHAVIOUR OF SERICIN. VI.*

By Hideo KANEKO.

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Part II.

COLLOIDAL BEHAVIOUR OF SERICIN A AND SERICIN B.

Sec. I. The Solubility of Sericin A and Sericin B.

Sericin A and sericin B, obtained by the fractional precipitation from the sericin solution with ammonium sulphate, differ in many properties from the natural sericin existing on the cocoon fibers. At the ordinary temperature the precipitation is accompanied by slight chemical change and is irreversible. Precipitated sericins are only very slightly soluble in cold water, and their solubilities and degrees of dispersion increase remarkably on both sides of the isoelectric point and also in dilute salt solutions. While sericin B is white, sericin A has a slightly gray colour. The solubility of sericin A is diminished more easily by heat or by the action of air than that of sericin B.

(1) **Solubility of the Precipitated Sericins in Alkalis and Acids.** The chemical constitution of the sericin molecule decides the general properties of sericin. The most active groups in the molecule are the basic amino-group and the acid carboxyl-group. So hydrogen- and hydroxyl-ions have a

* Continued from p. 421 of this volume.

predominating influence both on the solubility of sericin in water and on the physico-chemical properties of its solution. The solubility of proteins depends generally on the quantity present. Such an anomalous solubility of sericin was investigated by K. Kondo, and I also noticed it with sericin A and sericin B. The definite quantities of sericin A or B were taken in small conical flasks containing 100 c.c. of 0.005 mol NaOH solution, and the flasks were frequently shaken and left in a thermostat of 14°C. for 48 hours. The nitrogen contents of the solutions were determined after treating them by a centrifuge.

The solubility of precipitated sericins in dilute alkali solutions increases first with increasing quantity of sericin, reaching a maximum point, and then diminishing gradually. Sericin A is less soluble in alkali than sericin B.

(a) **Effect of pH on Solubility.** Fairbrother and Swann⁽⁵³⁾ showed that, with increasing concentration of either acid or alkali, more and more gelatin goes into solution, that acid or alkali disappears from the solution, and that there is a definite minimum point of solubility in very dilute acid.

(i) **Solubility in Alkali.** The precipitated sericin (1 g.) was put in 100 c.c. of alkali solutions having various hydrogen-ion concentrations under

the same conditions described above, and the quantity of dissolved nitrogen was determined by Kjeldahl method and pH value of the solutions by the electrical method, (Table 91).

Table 91.
Solubility of Sericins in NaOH Solution
at 20°C.

Original NaOH solution pH	Sericin A		Sericin B	
	pH (2 days after)	Dissolved quantity (%)	pH (2 days after)	Dissolved quantity (%)
5.7	6.7	7.96	6.7	9.95
7.2	6.8	8.18	6.8	10.17
11.0	7.4	9.75	7.2	11.15
12.0	8.5	12.38	8.4	12.82

As observed by Fairbrother and Swann, the solubility (g./100 c.c.) of sericin A or sericin B in the alkali solution increases with increasing concentration of alkali and at the same time alkali disappears from the solution, that is, the pH

value diminishes by the addition of sericin.

The precipitated sericins were found slightly more soluble in KOH solution than in NaOH solution.

(53) Fairbrother and Swann, *J. Chem. Soc.*, **121** (1922), 1237.

(ii) **Solubility in Acid.** Under the same conditions described above, I determined the solubilities of the precipitated sericins in acid solutions having various hydrogen-ion concentrations, (Table 92).

Table 92. Solubility of Sericins in HCl Solution.

Original HCl solution pH	Sericin A			Sericin B		
	pH (2 days after)	Dissolved quantity (%)	V	pH (2 days after)	Dissolved quantity (%)	V
3.8	6.4	7.74	2.8	6.3	9.51	4.0
3.4	6.0	7.07	2.6	5.9	8.85	3.4
3.0	5.4	6.25	2.0	5.3	7.60	2.9
2.75	4.7	5.75	1.9	4.7	7.32	2.7
2.4	4.6	5.67	1.7	4.6	7.35	2.7

V: the quantity (c.c.) of 0.1 N HCl combined with sericins.

The existence of a well-marked point of minimum solubility over a narrow range of hydrogen-ion concentration is characteristic of most proteins, and the point of minimum solubility is pH 4.5 for sericin A and pH 4.7 for sericin B, as shown in Fig. 39.

On account of slight denaturation on precipitating sericins, their isoelectric points are displaced to the more alkaline side than that of natural sericin.

The point of minimum solubility in sulphuric acid solution was found pH 4.4 for sericin A and pH 4.6 for sericin B.

The results are summarized as follows:

(a) When precipitated sericins are added to the acid or alkali solution, acid or alkali disappears from the solution, sericin combining stoichiometrically with it.⁽⁵⁴⁾

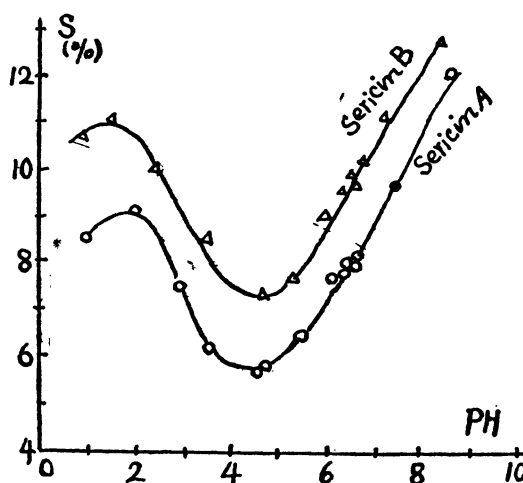


Fig. 39.

(54) J. Errera, *Compt. rend.*, **193** (1931), 1347.

(b) The solubility of sericin precipitated with $(\text{NH}_4)_2\text{SO}_4$ increases with increasing concentration of acid or alkali, reaching a maximum point, and then falling gradually.

(c) The precipitated sericins possess a minimum solubility near pH 4.5, which corresponds to the isoelectric point of natural sericin.

(d) The solubility of sericin A in dilute acid or alkali solution is less than that of sericin B.

(e) Both sericin A and sericin B are more soluble in HCl solution than in H_2SO_4 solution.

(b) **Effect of the Temperature on the Solubility.** The solubility of sericins depend on the hydrogen-ion concentration and also on the temperature as it is well known. The effect of the temperature on the solubility of sericins in HCl solution having pH 2.4 is shown in Table 93, where constant K was obtained by calculation from the formula $\log S - \log A = K \log t$ or $S = At^K$, S being the solubility of sericins, t the temperature, and A constant.

Table 93.

	Below 30°C.		Above 30°C.	
	K	$\log A$	K	$\log A$
Sericin A	0.027	0.685	0.024	-2.00
Sericin B	1.73	0.740	1.54	-1.55

Near 30°C. the variation in solubility of the precipitated sericins is remarkable, while the solubility of the natural sericin varies rapidly near 60°C.

(c) **Solubility in the Solutions of Sodium Salts of Organic Acids.** The precipitated sericin (1 g.) was introduced into 100 c.c. of 0.01 mol salt solution, and the solubility was determined at 20°C. after 48 hours (Table 94.).

Table 94.

Salt	Sericin A	Sericin B	Salt	Sericin A	Sericin B
HCO_2Na	10.01%	10.65%	$\text{C}_3\text{H}_7\text{CO}_2\text{Na}$	10.20%	9.51%
$\text{CH}_3\text{CO}_2\text{Na}$	9.98	10.01	$\text{C}_4\text{H}_9\text{CO}_2\text{Na}$	10.50	9.06
$\text{C}_2\text{H}_5\text{CO}_2\text{Na}$	10.01	9.73	$\text{C}_{17}\text{H}_{33}\text{CO}_2\text{Na}$	17.91	15.26

With increasing number of carbon atoms in the molecule of the salts, the solubility of sericin A increases slightly, while that of sericin B dimi-

nishes as is the case with the natural sericin and gelatin. In the solution of salts of higher fatty acids, such as oleate, sericin dissolves considerably as it is well known.

(2) **Buffer Capacity of Sericin A and Sericin B.** One gram of sericin A or sericin B was dissolved in a solution containing 1 milli-mol NaOH and the resulting solution was made up to 1 liter. Twenty c.c. of this solution were mixed with x c.c. of 0.01 N HCl and $(30-x)$ c.c. of distilled water. pH was determined colorimetrically when there was no interference by colour reactions, and by the quinhydrone electrode, when there was such.

The buffer capacity of precipitated sericins is approximately equal to that of gelatin, and sericin A and sericin B have nearly the same buffer capacity as shown in Fig. 40, where dots are the values for sericin A (sericin B shows nearly the same values), crosses those for gelatin, and v denotes the number of c.c. of 0.01 N HCl added to 20 c.c. of the sericin solution. This fact leads to the conclusion that the isoelectric point of sericin A is near that of sericin B. In fact, the isoelectric points of sericin A and sericin B were found respectively pH 4.1 and pH 4.2 by comparing the degree of turbidity of their solutions.

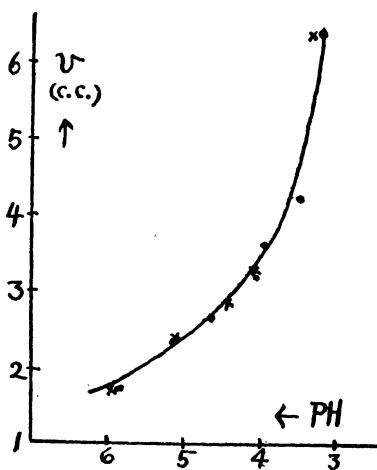


Fig. 40.

Sec. II. The Electric Cataphoresis of Precipitated Sericins.

The isoelectric point of a protein must be the point at which an equal number of diffusible anions and cations are present owing to the dissociation of the protein complex, and under this condition the protein presents the amphoteric ion $R \begin{matrix} \text{NH}_3^+ \\ \text{COO}^- \end{matrix}$. In acid solutions the ionization of the carboxyl-group is suppressed while the ionization of the ammonium-group is increased. The protein becomes then positive complex ion. In alkali solution or in solutions having a higher pH than that of the isoelectric point, the ionization of the ammonium-group is suppressed while the ionization of the carboxyl-group is increased. The protein is, then, electronegative.

One gram of sericin A or sericin B was dissolved in a solution containing 1 milli-mol NaOH and the solution was treated in the same manner as described before. The cataphoresis measurements were made by the microscopic method as shown previously. The results are shown in Tables 95, 96 and Fig. 41.

Table 95.

Cataphoretic Velocity of Sericin A.

Vol. of $\frac{N}{10}$ HCl added (c.c.)	pH		$U(\mu/\text{sec. per 1 volt/cm.})$	$\zeta(\text{m.v.})$
1.3	4.7	slightly milky	-0.701	-1.708
1.4	4.5	milky, ppt. later	-0.565	-1.376
1.5	4.35	" "	—	—
1.6	4.2	" "	-0.306	-0.743
1.7	4.05	most ppt.	—	—
1.8	3.95	ppt.	+0.306	+0.748
1.9	3.78	"	—	—
2.0	3.7	milky, ppt. later	+0.391	+0.952
2.1	3.6	slightly milky	—	—

Table 96.

Cataphoretic Velocity of Sericin B.

Vol. of $\frac{N}{10}$ HCl added (c.c.)	pH		$U(\mu/\text{sec. per 1 volt/cm.})$	$\zeta(\text{m.v.})$
1.3	4.7	very slightly milky	-0.896	-2.163
1.4	4.5	milky, ppt. later	-0.767	-1.844
1.5	—	ppt.	—	—
1.6	4.25	most ppt.	0.00	0.00
1.7	—	ppt.	—	—
1.8	4.05	slightly milky	+0.283	+0.683
1.9	3.7	very slightly milky	—	—
2.0	3.6	" " "	—	—

The electromotive potential developed on the interface between a protein particle and water may vary with *pH* of the solution. The charged protein particles can be precipitated from solution under such conditions as reduce the potential to less than 1.5 milli-volts. This reduction can be brought about by dilute solutions of salts, the active precipitating ion being the one carrying the opposite charge to the protein ion, and the effect being proportional to the valency of the ion as already shown.

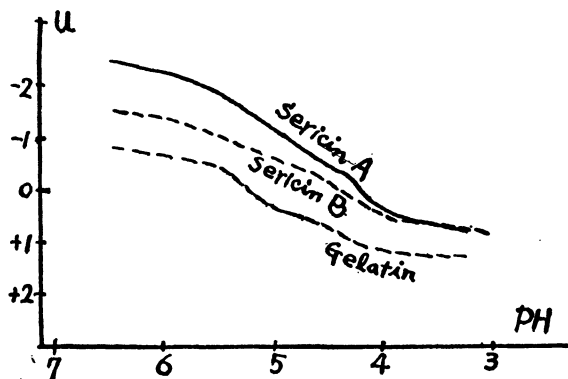


Fig. 41.

Debye and Hückel's formula indicates that, for a given potential difference *E*, there is a direct proportionality between the potential of the double layer and the cataphoretic velocity, *U* (μ /sec.):

$$\zeta = \frac{6\pi\eta U}{ED}.$$

From Table 94 and 95 it can be found that the isoelectric points of sericin A and sericin B in very dilute alkaline solutions exist respectively near *pH* 4.1 and *pH* 4.25, and that the rate of migration of sericin A is slightly greater than that of sericin B.

The flattened form of the sericin curves in Fig. 41 indicates that sericin remains electrokinetically very sluggish over the whole range. This leads us to the suspicion that sericin, like gelatin, is less reactive both as an acid and as a base than egg albumin. M. Samec⁽⁵⁵⁾ showed that amylopectin possesses a greater cataphoretic velocity than any other component of starch though it is the most hydrated.

Effect of Salts. The cataphoretic velocity of sericin is influenced by the presence of salts as well as by *pH* (Table 97).

The influence of salts on the surface potential of sericin A is shown in Fig. 42. Small quantities of an electrolyte having a monovalent cation raises the boundary charge. Since this increase is due to the negative ion,

(55) M. Samec, *Kolloid-Beihfte*, **33** (1931), 269-278.

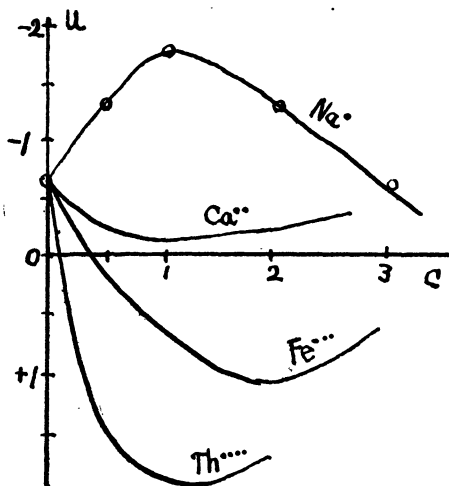


Fig. 42.

the influence of the latter in minute concentration seems to exceed the discharging effect of a monovalent cation. In the case of a divalent or trivalent cation, however, the discharging effect of that ion comes immediately into force.

Sec. III. Some Properties of Sericin A and Sericin B.

(1) **The Gold Number.** The gold numbers of sericin A and sericin B in N/3000 NaOH solution are given in Table 98.

Table 98.

Conc. (%)	Sericin A	Sericin B
0.10	0.025	0.035
0.16	0.023	0.0295
0.22	0.0185	0.024
0.30	9.014	0.018

Sericin A and sericin B swell in various solutions and liquids. The specific gravity of sericin measured by the usual submersion method will, therefore, vary with the liquids used. So the true specific gravity cannot be obtained, but the apparent one depending on the nature of the liquid.

Table 97.

Salt	Sericin A		Sericin B	
	$U(\mu/\text{sec.})$	$\zeta(\text{m.v.})$	$U(\mu/\text{sec.})$	$\zeta(\text{m.v.})$
NaCl	-1.797	-4.501	-1.972	-4.873
KCl	-2.01	-5.032	-2.386	-5.895
CaCl ₂	-0.122	-0.306	-0.487	-1.203
MgCl ₂	-0.378	-0.946	-0.235	-0.5806
AlCl ₃	+0.590	+1.470	+0.127	+0.3119
FeCl ₃	+0.500	+1.245	+0.368	+0.906
Th(NO ₃) ₄	+2.010	+5.032	—	—

The concentration of the salt solutions is 0.001 mol and the volume added is 1.0 c.c.

The protective action of sericin A is greater than that of sericin B under the same conditions.

(2) The Apparent Specific Gravity.

It is known that in most hygroscopic materials a contraction in total volume occurs during adsorption of water, and this is probably true for sorption in general. When such occurs, an *apparent* density will be obtained which is greater than the *true* density.

Table 99.

App. density	Liquid used	Author
1.361	Hot water	Müller
1.350	Cold water	J. Kubota ⁽⁵⁶⁾
1.33	Benzine	—

Further, from the value of the apparent density we can presume the order of swelling of sericin in liquids. In an active solvent in which sericin swells, the apparent specific gravity is greater than in an inactive solvent. This fact can be seen for the apparent density of raw silk (Table 99).

The apparent density of raw silk depends on the quantity of sericin remaining on the silk fiber, and on the liquid used. The apparent density of sericin A and sericin B is shown in Table 100.

Table 100.

Apparent Specific Gravity of Sericins (15°C.)

Liquid used	Sp. gr. of liquid (15°C)	Sp. gr. of sericin A	Sp. gr. of sericin B	Diff.
Acetone (1)	0.8071	1.412	1.339	0.073
„ (2)	0.7989	1.404	1.322	0.082
C ₂ H ₅ OH	0.7955	1.3947	1.3690	0.0257
HCOOH	1.1640	1.374	1.357	0.017
Pyridine	1.0004	1.370	1.353	0.017
CH ₃ COOH	1.0713	1.370	1.368	0.002
C ₆ H ₅ NO ₂	1.0209	1.3688	1.328	0.0408
CH ₃ OH	0.8019	1.366	1.353	0.013
C ₆ H ₆	0.8848	1.375	1.344	0.013
Water	1.000	1.356	1.309	0.047
C ₆ H ₄ (CH ₃) ₂	0.8642	1.283	1.265	0.018

(1) Merck's acetone.

The active solvents in which precipitated sericin swells are acetone, ethyl alcohol, formic acid, and pyridine. Benzene and xylene which have no or small permanent dipole moment are inactive.

Nitrobenzene, methyl alcohol, and acetic acid are moderately active solvents for sericin. It was impossible to determine the true density of the powdered sericin.

The reciprocal values of densities of proteins are shown in Table 101.

(56) J. Kubota, *Bull. Sericul. and Silk Ind. Japan*, **5** (1932), 68-69.

Table 101.

Protein	1/d	Protein	1/d
Sericin A	0.736 (in benzene)	Gelatin	0.724
Sericin B	0.744 (,, ,)	Egg-albumin	0.735
Fibroin	0.740 (in water)	Serum albumin	0.735

(3) Colour Reactions of Sericin A and Sericin B.

Table 102.

Solution of Precipitated sericins in N/10 NaOH.

Colour reaction	Sericin A	Sericin B
Engel's reaction	none	none
Million's reaction	given	given (deeper red)
Arginine reaction	given (5.95%)*	given (3.50%)*
May and Rose's and Neubauer Rhode's reaction	given faintly	none
Sulphur reaction	given faintly	given faintly
Histidin reaction	given	given
Biuret reaction	violetish red	violetish red
Xanthoprotein reaction	given	given

* By colorimetry.

Recently the existence of tryptophane in sericin has been reported by Abderhalden.⁽⁵⁷⁾

The Biuret Reaction of Sericin A and Sericin B. The red tinge of the biuret colour reaction of sericin sol has qualitatively an intimate relation with the quantity of sericin in it, but the colour is influenced by the presence of other substances in the cocoon layer. So it was impossible to determine quantitatively the degree of "kaijo" of cocoons by the colour of the biuret reaction of sericin sol.

(57) Abderhalden, *Z. physiol. Chem.*, **202** (1931), 37, *ibid.*, **207** (1932), 141-146.

(4) **Fluorescent Colours of Sericin A and Sericin B Solutions under the Ultraviolet Light.** When the sericin A and sericin B solutions in dilute alkali are exposed to the ultraviolet light, both give a slight yellow fluorescence. If a minute amount of glycocoll which is contained in the solution of the natural sericin and gives slight violet fluorescence be added to the sericin solutions, there is no variation in fluorescent colour of the sericin A solution, while the sericin B solution gives immediately a brilliant violet fluorescence. If the sericin A and sericin B solutions contain small amounts of aspartic acid, both give the same violet fluorescence. The fluorescent colours produced by the sericin solutions are influenced by the presence of a minute quantity of salts. From these results it can be seen that the fluorescent colours depend on the impurities adsorped or occluded in the cocoon layers which have close relation with the variety of cocoons, and on the proportion of sericin A and sericin B which is also intimately related to the variety.

(5) **Transformation from Sericin A to Sericin B.** Sericin A is more sensitive to heat than sericin B. So sericin A is transformed gradually into sericin B by heating it in drying apparatus, by steaming or by heating its solution in a flask.

Sec. IV. The Swelling of the Sericin A and Sericin B.

It will be interesting to note that substances like gelatin, casein, sericin, and starch, which are proved to be amorphous by X-ray analysis of Debye and Scherrer are the very substances that show the phenomenon of swelling. But the stretched sericin A will be shown to be crystalline by X-ray examination as done in the case of fibroin.

Sericin, when dry, is hygroscopic and it contains usually about 10% water. The sericin immersed in water gradually swells, or imbibes water. The swelling of the precipitated sericin in water and in the solutions of acids was investigated by M. Oku,⁽⁵⁸⁾ who showed that the swelling of the precipitated sericin in very dilute acid solutions possesses a minimum point in 1/1024 mol HCl or H₂SO₄ solution, and that it swells more in HCl solution than in H₂SO₄ solution.

The swelling of proteins belongs to complex phenomena and it depends on the expansion of colloidal micellæ, and on the adsorption and imbibition of liquid molecules or ions. This phenomenon of swelling has naturally a close relation to the "kaijo" of cocoons. Precipitated sericin (0.2 g.) was

(58) M. Oku, *Reports Gunze Phys. Chem. Lab. Japan*, **4** (1929), 15-22.

put in centrifuge tubes with scales, mixed with 10 c.c. of water or a salt solution, and then left to stand for 24 hours at 20°C. After the equilibrium was reached it was treated in a centrifuge for 30 minutes and the increase in volume of the sericin referred to the original was taken as expressing the comparative degree of the swelling.

(1) The Swelling of Sericins in the Solutions of Organic Sodium Salts.

(a) Sericin A. I used the sodium salts, for their anions are the least surface capillary active (Table 103 and Fig. 43).

Table 103.

	C_m	O
HCO ₂ Na	0.50	0.73
CH ₃ CO ₂ Na	0.33	2.84
C ₂ H ₅ CO ₂ Na	0.25	8.93
n-C ₃ H ₇ CO ₂ Na	0.21	19.6
n-C ₄ H ₉ CO ₂ Na	0.125	68.5

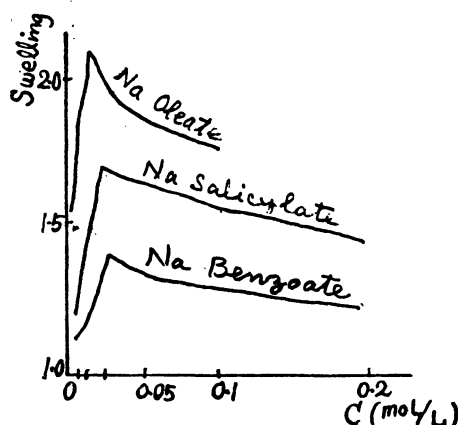


Fig. 43.

In the sodium salt solutions of fatty acids the concentration for the minimum swelling of sericin A, C_m , decreases with increasing number of carbon atoms in their molecules and it has the following relation with capillary activity of the fatty acids, O ,

$$\log O = 3.0 - 8.2 C_m .$$

The maximum swelling in the solution of oxalate or salt of an oxy-acid is coincident with the minimum point in the solutions of sodium salts of fatty acids, and at the concentration of 2 mol and in concentrations less than 0.125 mol the arrangement of the anions according to the type and the intensity of their influence on swelling leads to the Hofmeister series: citrate < tartrate < acetate. As the precipitated sericin adsorbs strongly the anion of sodium oleate, it has a maximum point of swelling in very low concentration of the salt (0.012 mol).

The relation between the concentration of the minimum swelling of sericin B and the number of carbon atoms of the salts of fatty acids was

contrary to the case of sericin A. The results were similar to those of their solubilities in the solutions of the same salts.

Taking the swelling of the precipitated sericin in distilled water at 20°C. as 100, the effects of salts on swelling are shown in Table 104.

Table 104. (Sericin A).

Mol	2	1	0.5	0.25	0.125	0.0625	0.0312
HCO ₂ Na	122.5	98.4	77.4	85.5	87.1	93.5	
CH ₃ CO ₂ Na	114.5	98.4	83.8	80.6	101.6	109.6	—
C ₂ H ₅ CO ₂ Na	150.0	132.2	104.8	98.6	109.6	130.6	—
n-C ₃ H ₇ CO ₂ Na	117.7	116.1	112.9	108.0	111.2	114.5	—
n-C ₄ H ₉ CO ₂ Na	—	145.1	119.3	112.9	101.6	106.4	109.6

The numbers less than 100 mean contraction in the solutions. In general sericin B swells more in the solutions of these salts than sericin A.

(2) **Swelling in the Solutions of the Sodium Salts of Inorganic Acids.** In the solutions of capillarily inactive sodium salts of inorganic acids sericin A and sericin B swell as well as in the solutions of capillarily active organic salts. But the concentration of the maximum swelling is greater than in the case of organic salts.

(3) **Effect of Acids and Bases.** The swelling of both sericins depends remarkably on the pH of the solutions as it is well known, and the minimum swelling of sericin A in HCl solutions corresponds to pH 3.75. Different acids causes different degrees of swelling.

Loeb (1922) considered that swelling was affected not only by the hydrogen-ion concentration, but also, in acid solutions, by the valency of the anion. Sericin A and sericin B swell considerably in a very dilute alkali solution and in concentrations higher than 1/40 mol NaOH the former disperses partly into solution.

The swelling of sericins in solutions of HCl and of NaOH is shown in Fig. 44. The acid curve rises sharply to the maximum at an external pH of 3.0; the alkaline curve rises slowly at first. The isoelectric point of sericin A exists on the more acid side than that of sericin B as frequently described.

(4) **Effect of Temperature.** The variation in swelling of sericins with rising temperature is shown in Fig. 45, where log *S* is given by the equa-

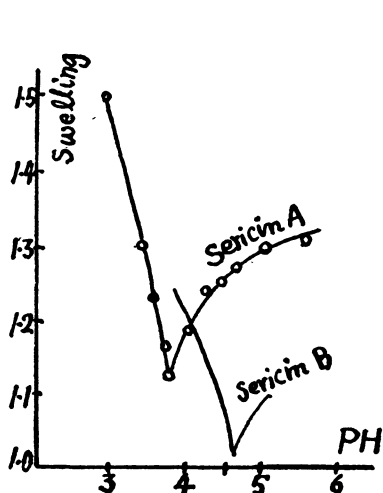


Fig. 44.

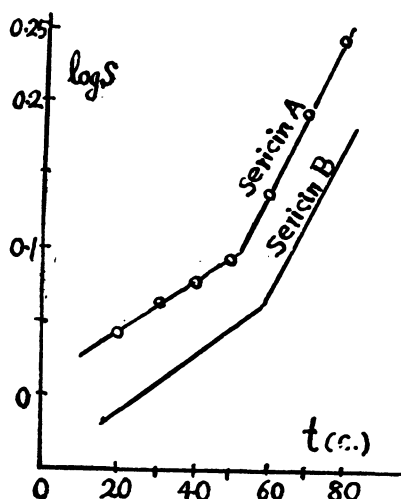


Fig. 45

tion : $\log S = A + Bt$ or $S = A'e^{Bt}$, where A and B are constants, the former depending on pH and on the state of sericin, and the latter on the state only. For example, $\log S = 1.33 + 0.005 t$ (below 50°C.), and $\log S = 1.54 + 0.14 (t - 50)$ (above 50°C.) for sericin A at pH 4.6. The abrupt change at 50°C. caused by the rapid transformation of gel into sol can also be seen in other properties.

Lloyd⁽⁵⁹⁾ showed that the quantity of absorbed water in gelatin is proportional to the square of temperature at low temperatures. If the quantity of adsorbed water be proportional to the increase in volume of sericin, the swelling may be proportional to the square of temperature. Such relation can be found in the results of this experiment.

(To be continued.)

(59) Lloyd, *Biochem. J.*, **21** (1929), 21, 1352; *ibid.*, **22** (1928), 1007; *ibid.*, **24** (1930), 1460; *ibid.*, **25** (1931), 1580.

DIE ZWEIDIMENSIONALE ZUSTANDSGLEICHUNG UND DER BAU VON GRENZFLÄCHENSCHICHTEN.*

Von Bunichi TAMAMUSHI.

Eingegangen am 14. Juli, 1934. Ausgegeben am 28. November, 1934.

Teil II. Die Oberflächenschicht reiner Flüssigkeiten.

1. Die Zustandsgleichung der Oberflächenschicht reiner Flüssigkeiten.

Die Ansicht, dass an der Oberfläche dielektrischer Flüssigkeit eine durch die Molekularkräfte hervorgebrachte Orientierung von Molekülen bestehe, ist besonders von Lenard,⁽³⁷⁾ Langmuir⁽³⁸⁾ und Harkins⁽³⁹⁾ vertreten worden. Die Langmuir-Harkinssche Vorstellung, dass sich solche Flüssigkeitsmoleküle, die sowohl nonpolare wie polare Gruppen enthalten, z. B. Fettsäuren an der Oberfläche derart richten, dass die nonpolare Gruppe ($-\text{CH}_3$) an der Oberfläche nach aussen gerichtet, die stark polare Gruppe ($-\text{COOH}$) nach dem Flüssigkeitsinnern gerichtet steht. Tatsächlich konnte man, in Übereinstimmung mit dieser Vorstellung, zeigen, dass die Oberflächenspannung bzw. die gesamte Oberflächenenergie der homologen organischen Flüssigkeiten (Alkohole, Fettsäuren) unabhängig von der Molekulargrösse gleichwertig ist;⁽⁴⁰⁾ die Oberfläche der homologen Flüssigkeiten verhalten sich deshalb als ob sie nur durch die inaktive Gruppe ($-\text{CH}_3$) gebildet wäre. Es wird also wohl erwartet, dass die Moleküle auch an der Oberfläche reiner Flüssigkeiten, ganz analog der adsorbierten Schicht auf Wasser, stabartig stehen und zwar bei der kurzen Reichweite der Molekularkräfte wird eine derartig orientierte Schicht sich an der Oberfläche monomolekular bilden,⁽⁴¹⁾ wenn auch die thermische Bewegung der Moleküle dagegen stets störend wirkt. Es scheint dann berechtigt, auch für die Oberfläche reiner Flüssigkeiten analog der adsorbierten Schicht eine zweidimensionale Zustandsgleichung aufzustellen, die im folgenden formuliert wird.

* Die Fortsetzung aus S. 393 dieses Bandes.

(37) Lenard, *Sitzungsber. d. Heidelberger Akad. d. Wiss. Math. Natw. Kl.*, 1914, 27, 28, 29.

(38) Langmuir, *J. Am. Chem. Soc.*, **38** (1916), 2231; **39** (1917), 1848.

(39) Harkins u. Mitarbeitern, *J. Am. Chem. Soc.*, **39** (1917), 354; 541; **42** (1920), 700; **43** (1921), 35; **44** (1922), 653.

(40) Hunten u. Maas, *J. Am. Chem. Soc.*, **51** (1929), 153.

(41) Vgl. Einstein, *Ann. Physik*, (4), **34** (1911), 165.

Man nimmt an, dass das Flüssigkeitsmolekül eigentlich an der Oberfläche die laterale freie Beweglichkeit besitzt, die aber durch die auf das Molekül gleichzeitig wirkenden starken Kohäsionskräfte weitgehend gehindert wird. Durch die Differenz dieser zwei Effekte

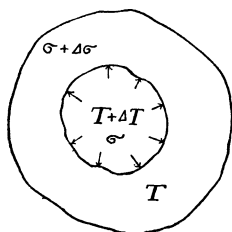


Fig. 6.

wird dann der messbare äussere Oberflächendruck angegeben. Man denkt sich nun auf der Oberfläche zwei Flächenteile, die sich jedes für sich in der Temperatur T und $T + \Delta T$ befinden und mit einer geschlossenen Linie voneinander begrenzt sind. In Wirklichkeit können solche Flächenteile von verschiedener Temperatur offenbar nicht im Gleichgewicht sein, aber es wäre doch gestattet, dies begrifflich anzunehmen. Nun hat der Flächenteil $T + \Delta T$ die

Oberflächenspannung σ und der Flächenteil T die Oberflächenspannung $\sigma + \Delta\sigma$ und somit wirkt die nach dem Flächenteil T hinziehende Kraft $d\sigma$ auf das Linienelement der Grenze, infolgedessen versucht sich der Teil $T + \Delta T$ nach aussen auszudehnen. Bezeichnet man diese Ausdehnungskraft (pro Linienelement) mit $d\Pi$, so wird :

$$d\Pi = -d\sigma .$$

Integriert dies von der tiefsten Temperatur T_0 bis zur Messungstemperatur T , so ergibt sich :

$$\Pi = \int_{T_0}^T d\Pi = - \int_{T_0}^T d\sigma = \sigma_0 - \sigma , \quad (1)$$

wo σ_0 die Oberflächenspannung in T_0 , und σ die Oberflächenspannung in T bedeutet. Angenommen ist hier, dass T_0 eine solche Temperatur ist, bei der keine thermische Bewegung mehr stattfindet, so würde σ_0 einen rein statischen Anteil der Oberflächenspannung darstellen. Der wirkliche Wert von σ_0 ist aber keineswegs zu ermitteln bei unseren gegenwärtigen unzulänglichen Kenntnisse über die Natur der Molekularkräfte. Ich nenne hier σ_0 die statische Oberflächenspannung.

Nun bedeutet Π den Oberflächendruck, mit dessen Hilfe wird die Zustandsgleichung der Flüssigkeitsoberfläche analog der adsorbierten Schicht mittels der Virial-Methode abgeleitet. Nimmt man auch hierbei zwischen den Molekülen eine Kraft in der Form $-\frac{\partial E}{\partial r}$ an, so wird die allgemeine Zustandsgleichung für ein Molekül: (Vgl. I. 4.)

$$\Pi\omega = \frac{1}{2}m v^2 - \frac{1}{2}r \frac{\partial E}{\partial r} , \quad (2)$$

wobei ω die Fläche eines Moleküls bedeutet. Verwendet man hierfür den Energie-Gleichverteilungssatz, so bekommt man :

$$\Pi\omega = kT - \frac{1}{2}r \frac{\partial E}{\partial r},$$

wo k die Boltzmannsche Konstante ist. Summiert man diese Gleichung über alle Paare der Moleküle in der Molaroberfläche der Flüssigkeit, unter Berücksichtigung :

$$\Omega = (Nv)^{\frac{2}{3}} \quad \text{und} \quad v^{\frac{2}{3}} = \omega,$$

wo N die Loschmidtsche Zahl und v das Volum eines Moleküls (kinetisch als Kugel betrachtet) bedeutet, so ergibt sich : (Vgl. I. 5.)

$$\Pi\Omega = N^{\frac{2}{3}}kT - \frac{1}{2} \frac{N^{\frac{4}{3}}\pi}{\Omega} \int_0^\infty r^2 \frac{\partial E}{\partial r} e^{-\frac{E}{kT}} dr.$$

Durch Integration folgt :

$$\Pi\Omega = N^{\frac{2}{3}}kT - \frac{N^{\frac{4}{3}}\pi}{\Omega} kT \int_0^\infty r(e^{-\frac{E}{kT}} - 1) dr, \quad (3)$$

oder

$$\Pi\Omega = N^{\frac{2}{3}}kT \left(1 + \frac{B}{\Omega}\right), \quad (4)$$

wobei für den zweiten Virialkoeffizient B eingesetzt ist :

$$B = N^{\frac{2}{3}}\pi \int_0^\infty r(1 - e^{-\frac{E}{kT}}) dr.$$

Diese Gleichung (4) ist die Zustandsgleichung der Oberflächenschicht reiner Flüssigkeiten, die im folgenden noch näher erläutert werden soll.

2. Theorie der Temperaturabhängigkeit der Oberflächenspannung.

Die Zustandsgleichung (4) :

$$\Pi\Omega = N^{\frac{2}{3}}kT + N^{\frac{2}{3}}kT \cdot \frac{B}{\Omega}$$

wird zweckmässigkeitshalber auch in die folgende Form gefasst :

$$\Pi\Omega = N^{\frac{2}{3}}kT - \phi(r), \quad (5)$$

wo $\phi(r)$ die Wechselwirkungsenergie (pro Molaroberfläche) zwischen den Molekülen darstellt. $\phi(r)$ ist im allgemeinen temperaturabhängig. Diese Beziehung ähnelt der Grundannahme in der van der Waals-Hulshofschen Theorie der Kapillarität,⁽⁴²⁾ indem sie besagt, dass der äussere manometrische Druck der Differenz zwischen thermischem und innerem Kohäsionsdruck gleich ist. Aber die hier angegebene Betrachtung unterscheidet sich im prinzipiellen von der van der Waals-Hulshofschen Theorie darin, dass sie in der Kapillarschicht nicht stetigen Dichtabfall sondern plötzlichen Dichtabfall annimmt. Die Gleichung (5) lässt sich schreiben:

$$(\sigma_0 - \sigma)\Omega = N^{\frac{2}{3}}kT - \phi(r),$$

oder

$$\sigma\Omega = \sigma_0\Omega - N^{\frac{2}{3}}kT + \phi(r). \quad (6)$$

Dies auf die Flächeneinheit gerechnet:

$$\sigma = \sigma_0 - n^{\frac{2}{3}}kT + \varphi(r), \quad (7)$$

wo $n^{\frac{2}{3}}$ die Molekülzahl in der Flächeneinheit, $\varphi(r)$ die Wechselwirkungsenergie pro Flächeneinheit bedeutet. Diese letzte Beziehung gibt eine Definition der Oberflächenspannung, nämlich: die Oberflächenspannung (Erg/qcm) ist gleich der Differenz der zwischenmolekularen und thermischen Energie, wobei die zwischenmolekulare Energie aus zwei Teilen besteht, ein rein statischer (σ_0) einerseits und ein temperaturabhängiger ($\varphi(r)$) andererseits.⁽⁴³⁾

Die Beziehung (6) bzw. (7) drückt gleichzeitig das Gesetz der Temperaturabhängigkeit der Oberflächenspannung aus, es enthält also die Eötvösche Formel als eine spezielle Folgerung. Für die kritische Temperatur (θ_0) der Flüssigkeit, wird σ gleich null und so folgt aus Gleichung (6):

(42) van der Waals-Kohnstamm, „Lehrbuch d. Thermodynamik“, I, (1927), S. 318.

(43) Diese Beziehung lässt sich mit den Born-Courantschen sowie Brillouinschen Beziehungen vergleichen. Nach Born und Courant (*Physik. Z.*, **14** (1913), 731) gilt:

$$\sigma = \sigma_0 - 2\pi \left(\frac{kT}{hc} \right)^2 kT \int_0^{x_m} \frac{x^2}{e^x - 1} dx,$$

und nach Brillouin (*Comp. rend.*, **180** (1925), 1248.)

$$\sigma = \sigma_0 - \frac{9}{4} \frac{NkT}{S_m},$$

wo, in den beiden Beziehungen, σ_0 den statischen Bestandteil der Oberflächenspannung und das zweite Glied in der rechten Seite eine Funktion der Temperatur darstellt.

$$\sigma_0 = \frac{N^{\frac{2}{3}} k \vartheta_0}{\Omega},$$

unter der Bedingung, dass auch der Virialkoeffizient B bzw. $\Phi(r)$ für die kritische Temperatur gleich null gesetzt werden kann. Dies in Gleichung (6) eingesetzt, so ergibt sich :

$$\sigma \Omega = N^{\frac{2}{3}} k (\vartheta_0 - T) + \Phi(r), \quad (8)$$

oder

$$\sigma \Omega = N^{\frac{2}{3}} k \left\{ 1 + \frac{\Phi(r)}{N^{\frac{2}{3}} k (\vartheta_0 - T)} \right\} (\vartheta_0 - T). \quad (9)$$

Setzt man weiter :

$$N^{\frac{2}{3}} k \left\{ 1 + \frac{\Phi(r)}{N^{\frac{2}{3}} k (\vartheta_0 - T)} \right\} = K \quad (10)$$

ein, so wird :

$$\sigma \Omega = K (\vartheta_0 - T),$$

was die Eötvössche Formel wiedergibt, wo K aber nicht mehr eine einfache Konstante, sondern eine Funktion ist, die im allgemeinen von Stoff zu Stoff verschieden und auch von der Temperatur abhängig sein soll.

Bevor ich auf die Analyse dieser Gleichungen eingehe, möchte ich hier einiges über die Geschichte des Eötvösschen Gesetzes berichten. Das Gesetz, das meist in die Form :

$$\sigma V^{\frac{2}{3}} = K (\vartheta_0 - T) \quad (11)$$

gefasst wird, wurde zuerst von Eötvös⁽⁴⁴⁾ rein empirisch aufgestellt, wo V das Molarvolum und K eine Konstante bedeutet, die weitgehend von der Flüssigkeit unabhängig war. Diese Formel wurde dann von Ramsay und Shields⁽⁴⁵⁾ eingehend geprüft, sie gaben eher der empirischen Beziehung die folgende Form :

$$\sigma V^{\frac{2}{3}} = K' (\vartheta_0 - T - \tau), \quad (12)$$

wo K' eine Konstante ist ; τ ist der kleine Betrag (6°) den man von der kritischen Temperatur abziehen muss, um den Schnittpunkt der σ , T -Geraden mit der T -Achse zu erhalten. Katayama⁽⁴⁶⁾ vermied diese willkürliche Konstante und stellte die Formel :

(44) Eötvös, *Wied. Ann.*, **27** (1886), 448.

(45) Ramsay u. Shields, *Z. physik. Chem.*, **12** (1893), 433.

(46) Katayama, *Science Rep. Tohoku Imp. Univ.*, **4** (1915), 373.

$$\sigma \left(\frac{M}{\rho_f - \rho_g} \right)^{\frac{2}{3}} = K''(\vartheta_0 - T) \quad (13)$$

auf, wo M das Molargewicht, ρ_f die Dichte der Flüssigkeit, ρ_g die Dichte des Dampfes, der mit der Flüssigkeit im Gleichgewicht steht und K'' eine Konstante bedeutet. Diese Formel hat die Vorzüge, dass sie nicht nur die empirischen Daten über einen grösseren Bereich der Temperatur wiedergibt, sondern auch, dass sie mit der Theorie der übereinstimmenden Zustände im Einklang steht.

Die Konstante K bzw. K' , K'' , in Gleichungen (11) bzw. (12), (13) erwies sich für eine Anzahl der Flüssigkeiten mit mittlerem Molargewicht, die man gewöhnlich als normal betrachtet, als konstant und zwar gleich dem Wert von rund 2. Aber nach den umfangreichen Untersuchungen von Walden,⁽⁴⁷⁾ Morgan,⁽⁴⁸⁾ Jaeger⁽⁴⁹⁾ und andern erwies sich sie keineswegs einfach als konstant. Eine Klasse von Substanzen, zu der z. B. Äthylalkohol, Essigsäure, Wasserstoff, Helium, geschmolzene Metalle und Salze gehören, hat kleineren Wert als 2, und eine andere Klasse, zu der meist hochmolekulare Verbindungen wie höhere Fettsäuren und ihre Glyceriden gehören, hat grösseren Wert als 2. Ausserdem verhält sich K nicht immer strikt temperaturunabhängig: der K -Wert von Wasser, Ameisensäure z. B. wächst mit steigender Temperatur an, während sich der K -Wert von Tetrachlorkohlenstoff, Azeton und den meisten hochmolekularen Verbindungen mit steigender Temperatur vermindert. Die Ansicht, dass die Moleküle der Flüssigkeiten, deren K -Wert in der Nähe von 2 liegt, normal d. h. nicht assoziiert seien, wird meistens als berechtigt angesehen. Die Ansicht, dass die Moleküle, deren K -Wert kleiner als 2 ist, assoziiert seien, bewährt sich in einigen Fällen (z. B. bei Wasser, Essigsäure, Äthylalkohol), aber in einigen andern Fällen (z. B. bei Wasserstoff, Helium, geschmolzenen Metallen und Salzen) nicht. Der Schluss, dass die Moleküle der Flüssigkeiten, deren K -Wert grösser als 2 ist, dementsprechend dissoziiert seien, wird offenbar widerlegt, da sie sich sonst normal verhalten. Die Ansicht, welche die Abweichung des K -Wertes von dem normalen Wert der Assoziation oder Dissoziation zuschreibt, hat also viel an Allgemeingültigkeit verloren.

Die erste molekularkinetische Grundlage des Eötvösschen Gesetzes verdankt man Madelung⁽⁵⁰⁾ und gleichfalls Born und Courant.⁽⁵¹⁾ Die letztgenannten Autoren übertrugen auf die Moleküle in der Oberflächenschicht

(47) Walden, *Z. physik. Chem.*, **65** (1908), 129, 257, usw.

(48) Morgan, *Z. physik. Chem.*, **65** (1908), 851, usw.

(49) Jaeger, *Akad. Amsterdam Versl.*, **23** (1914); *Z. anorg. allg. Chem.*, **101** (1917), 1.

(50) Madelung, *Physik. Z.*, **14** (1913), 729.

(51) Born u. Courant, loc. cit. unter (43).

der Flüssigkeit die Betrachtungen, die zuerst von Debye⁽⁵²⁾ auf die Moleküle fester Körper angewandt wurden, und sie gelangten zu einer mit der Eötvösschen Formel gleichdeutigen Formel, wo sich der Zahlenwert von K unter bestimmten Voraussetzungen ableiten lässt. Sie konnten auch den abnorm grossen Wert von K für hochmolekulare Verbindungen dadurch deuten, dass die grossen Moleküle dieser Substanzen nicht bloss als Ganze schwingen, sondern dass im Molekül vorhandene Atomgruppen bestimmte Schwingungsfreiheit haben. Brillouin⁽⁵³⁾ verfeinerte die Born-Courantsche Theorie, indem er in der Flüssigkeitsoberfläche einen dem Lichtdruck analogen Druck annahm. Inzwischen hat die Langmuir-Harkinssche Theorie der Orientierung von Molekülen entwickelt.⁽⁵⁴⁾ Der Umstand, dass die Orientierung und Gestalt von Molekülen mit der Abweichung des K -Wertes vom normalen Wert im Zusammenhang stehe, wurde besonders von Adam⁽⁵⁵⁾ in Betracht gezogen. Adam hat dabei das Eötvösschen Gesetz in der Zustandsgleichung:

$$H\omega = kT \quad (14)$$

wiedergegeben, indem er den Begriff des Oberflächendruckes einführte.

Die elektrische Theorie der Oberflächenschicht ist von Frenkel⁽⁵⁶⁾ und Jung⁽⁵⁷⁾ entwickelt worden. Jung hat die Eötvössche Formel abgeleitet, unter Zugrundelegung der Annahme, dass sich die Moleküle an der Oberfläche orientieren und dadurch ein inneres Feld entsteht. Es zeigt sich dabei, dass der K -Wert nur bei Substanzen mit sehr kleinem Dipolmoment temperaturunabhängig ist, während er bei Substanzen mit grossem Dipolmoment temperaturabhängig ist. Endlich wurde der Umstand, dass die mannigfaltig wirkenden Zwischenmolekularkräfte den Molekülverband beeinflussen und infolgedessen die komplizierte Temperaturabhängigkeit der Oberflächenspannung verursachen, hier und da nur andeutungsweise ausgesprochen.⁽⁵⁸⁾ Im folgenden soll gerade dieser letzt genannte Umstand, in bezug auf die oben angegebene Ableitung des Eötvösschen Gesetzes, besonders in Betracht gezogen werden. Die Betrachtungen bleiben übrigens mehr oder weniger formal, da unsere Kenntnisse über Molekularkräfte noch ungenügend sind.

(52) Debye, *Ann. Physik*, (4) **39** (1912), 789.

(53) Brillouin, loc. cit. unter (43).

(54) Langmuir u. Harkins, loc. cit.

(55) Adam, *Phil. Mag.*, (7), **8** (1929), 539.

(56) Frenkel, *Phil. Mag.*, (6), **33** (1917), 297; *Z. Physik*, **51** (1928), 232.

(57) Jung, *Z. physik. Chem.*, **123** (1926), 281.

(58) z. B. Freundlich, „Kapillarchemie“, Bd. 1. (1930), S. 52; Adam, „The Physics and Chemistry of Surfaces“, (1930), S. 158.

Wenn man die Eötvössche Formel in die Form :

$$\sigma\Omega = K(\vartheta_0 - T)$$

fasst, wobei

$$K = N^{\frac{2}{3}}k \left\{ 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} \right\},$$

oder

$$K = 0.981 \left\{ 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} \right\}$$

ist, so folgen für K verschiedene mögliche Werte unter den Bedingungen :

1. $\phi(r) > 0$

$$\text{a) } \phi(r) > N^{\frac{2}{3}}k(\vartheta_0 - T), \quad 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} > 2, \quad K > 2 \times 0.981.$$

$$\text{b) } \phi(r) = N^{\frac{2}{3}}k(\vartheta_0 - T), \quad 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} = 2, \quad K = 2 \times 0.981.$$

$$\text{c) } \phi(r) < N^{\frac{2}{3}}k(\vartheta_0 - T), \quad 1 < 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} < 2, \\ 0.981 < K < 2 \times 0.981.$$

2. $\phi(r) < 0$

$$\text{a) } |\phi(r)| < N^{\frac{2}{3}}k(\vartheta_0 - T), \quad 0 < 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} < 1, \\ 0 < K < 0.981.$$

$$\text{b) } |\phi(r)| = N^{\frac{2}{3}}k(\vartheta_0 - T), \quad 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} = 0, \quad K = 0.$$

$$\text{c) } |\phi(r)| > N^{\frac{2}{3}}k(\vartheta_0 - T), \quad 1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} < 0, \quad K < 0.$$

3. $\phi(r) = 0$

$$1 + \frac{\phi(r)}{N^{\frac{2}{3}}k(\vartheta_0 - T)} = 1, \quad K = 0.981.$$

Das Postulat 1) $\phi(r) > 0$ bedingt zwischen den Molekülen die Anziehungskräfte. Die Konstante K wird dann nicht nur immer grössere Werte als 0.981, sondern auch verschieden grosse Werte annehmen, je nach dem möglichen Verhältnis der Kohäsionsenergie zur Differenz der statischen und thermischen Energie. Das Postulat 2) $\phi(r) < 0$ bedingt dagegen die abstossenden Kräfte zwischen den Molekülen. K wird dabei kleiner als 0.981; er wird eventuell gleich null ausfallen. $K = 0$ fordert aber in der Eötvösschen Formel dass $\sigma = 0$ ist, sofern $T \neq \vartheta_0$ ist. Dass die σ , T -Gerade tatsächlich schon vor dem kritischen Punkt die T -Achse zu schneiden scheint, könnte also durch das Postulat 2) b) ermöglicht werden. Das Postulat 2) c) fordert $K < 0$ bzw. $\sigma < 0$, was aber in Wirklichkeit nicht möglich ist. Das letzte Postulat 3) $\phi(r) = 0$ bedingt keine temperaturabhängigen Molekularkräfte zwischen den Molekülen, wo K einen bestimmten Wert, nämlich $N^{\frac{2}{3}}k = 0.981$ hat, sofern $T \neq \vartheta_0$ ist. Wenn nun die Temperatur gleich der kritischen Temperatur ist, so wird sowohl $\sigma = 0$ sein, als auch $\phi(r) = 0$ sein (die erste Annahme). Dann wird K -Wert mathematisch anscheinend unbestimmt, sein Grenzwert wird aber null ergeben, wenn man die Bedingung:

$$\lim_{T \rightarrow \vartheta_0} |\phi(r)| = \lim_{T \rightarrow \vartheta_0} N^{\frac{2}{3}}k(\vartheta_0 - T) = 0$$

als gültig annimmt. Schliesslich scheint es also erfolgreich den abnormen K -Wert mittels den Molekularkräften zu deuten, indem man den grösseren K -Wert den Anziehungskräften und den kleineren K -Wert den Abstossungskräften zuordnet.

Nun war der abnorm kleine K -Wert von Wasserstoff, Helium, geschmolzenen Metallen und Salzen nicht begreiflich durch Assoziation und gerade in diesen Fällen hätte die Art des Molekülverbandes bzw. die Natur der Zwischenmolekularkräfte viel zu bedeuten. Es kommt wahrscheinlich zwischen Molekülen im flüssigen Wasserstoff oder Helium die van der Waalssche Kohäsion verhältnismässig nur in geringem Masse vor, wodurch der kleine K -Wert bei diesen Stoffen verständlich wird. Dagegen würden bei geschmolzenen Metallen und Salzen, in denen eher Atome oder Ionen existieren müssen, die abstossenden Kräfte zwischen ihnen zur Wirkung kommen, damit sich der noch viel kleinere K -Wert von diesen Substanzen verstehen lässt.

Der abnorme grosse K -Wert wäre den hohen Kohäsionskräften zwischen den Molekülen zuzuschreiben, was ja bei hochmolekularen Verbindungen im allgemeinen sehr wahrscheinlich ist. Man müsste aber bei hochmolekularen Verbindungen ausser den Zwischenmolekularkräften noch andere den K -Wert vergrössernd wirkende Faktoren, nämlich, Molekülzahl, Mole-

külgestalt, Molekularorientierung, Schwingungsfreiheit der Molekülgruppen usw. nennen. Der K -Wert ist dann eine recht komplizierte Funktion von diesen Faktoren, in denen die Zwischenmolekularkräfte immerhin als ein massgebender Faktor angesehen werden müssten.

Um sich davon noch besser zu überzeugen, betrachte ich unten die homologe Reihe der normalen Fettsäuren. Nach den Untersuchungen von Hunten und Maas⁽⁵⁹⁾ sind die K -Werte von den homologen Fettsäuren wie in folgender Tabelle:

Tabelle 6.

Stoff	K -Wert	$1-i$
Ameisensäure	0.90	0.00
Essigsäure	1.35	0.03
Propionsäure	1.53	0.15
Buttersäure	1.65	0.27
Capronsäure	2.04	0.57
Caprylsäure	2.12	0.54
Caprinsäure	2.36	0.65
Laurinsäure	2.56	0.77
Myristinsäure	2.80	0.79
Palmitinsäure	2.92	—
Margarinsäure	3.00	—
Stearinsäure	3.04	—

Der K -Wert wächst also beinahe regelmässig mit der sich vergrössern- den Kettenlänge an. Auffallender- weise steht dieses Anwachsen in naher Analogie zu dem Anwachsen des $1-i$ -Wertes bei den adsorbierten Schichten, der in der dritten Spalte zum Vergleich angegeben ist. (Teil I. Abs. 3) Sowohl das Anwachsen des $1-i$ -Wertes durch die mit der Ketten- länge zunehmenden Dispersionskräfte lässt sich begreifen, als auch das Anwachsen des K -Wertes, welches durch dieselbe Kräfte erklärt werden könnte. Es müsste aber natürlich hierbei auch der Einfluss von Asso- ziation bzw. Molekülzahl, Molekül- gestalt, Molekularorientierung und

Molekülschwingung in Rücksicht gezogen werden. Der kleine Wert von K für Säuren bis die Kohlenstoffzahl 4 ist ja wahrscheinlich der Assoziation zuzuschreiben. Die Schwingungsfreiheit der Molekülgruppen könnte für alle Glieder als gleichmässig angenommen werden. Die Molekülgestalt und Molekularorientierung beeinflussen hierbei allerdings den K -Wert, indem sie ihn vergrössern, aber sie scheinen nicht imstande, das charak- teristische Anwachsen vom K -Wert zahlenmässig wiederzugeben. So scheint es mir geglückt zu sein für diesen Fall den engen Zusammenhang des K -Wertes mit den Kohäsionskräften festzustellen.

Es wird nun auf die Veränderlichkeit des K -Wertes mit der Temperatur eingegangen. Der K -Wert in der Eötvösschen Formel ist eventuell recht konstant über einen grossen Bereich der Temperatur, aber er ist im allge- meinen nicht strikt unabhängig von der Temperatur und manchmal ver-

(59) Hunten u. Maas, loc. cit.

ändert sich der K -Wert auffallend mit der Temperatur. Der K -Wert von Wasser sowie von Essigsäure z. B. nimmt mit steigender Temperatur zu, wofür die Veränderlichkeit des Assoziationsgrades verantwortlich sein könnte. Auch der K -Wert von solchen normalen Substanzen wie Tetrachlorkohlenstoff, Äthylazetat und andern ist weitgehend temperaturabhängig, und zwar nimmt er mit steigender Temperatur ab. Dagegen haben hochmolekulare Verbindungen meist einen zu grossen und mit steigender Temperatur abnehmenden K -Wert. Bei anisotropen Flüssigkeiten verhält sich der K -Wert ganz charakteristisch; er wächst mit steigender Temperatur bis zu einem maximalen Wert an und dann vermindert er sich allmählich. Gerade in diesen Fällen hätte die Natur der Zwischenmolekularkräfte für die Temperaturabhängigkeit des K -Wertes viel zu bedeuten.

Die Veränderlichkeit des K -Wertes mit der Temperatur lässt sich nun auch aus der Zustandsgleichung (6) als ein natürlicher Schluss folgern. Rechnet man also die Zustandsgleichung:

$$\sigma\Omega = \sigma_0\Omega - N^{\frac{2}{3}}kT + \phi(r)$$

auf die Flächeneinheit, so ergibt sich:

$$\sigma = \sigma_0 - n^{\frac{2}{3}}kT + \phi(r),$$

wo $\phi(r)$ eine Funktion von Temperatur ist. Differenziert man dies nach T , so wird:

$$\frac{d\sigma}{dT} = -n^{\frac{2}{3}}k + \phi'(r).$$

Dies durch nochmalige Differentiation nach T , wird:

$$\frac{d^2\sigma}{dT^2} = \phi''(r).$$

Wenn also $\phi''(r)$ gleich null wäre, so würde $\frac{d\sigma}{dT} = \text{constans}$, demnach würde $\frac{d(\sigma\Omega)}{dT}$ constans, d. h. die Eötvössche Konstante K temperaturunabhängig sein. Wenn aber sonst $\phi''(r)$ nicht gleich null wäre, so würden folgende Möglichkeiten resultieren:

$$1) \quad \phi''(r) > 0 \quad \text{d. h.} \quad \frac{d^2\sigma}{dT^2} > 0. \quad (15)$$

$$2) \quad \phi''(r) < 0 \quad \text{d. h.} \quad \frac{d^2\sigma}{dT^2} < 0. \quad (16)$$

Der erste Fall bedingt, dass $\frac{d\sigma}{dT}$ mit steigender Temperatur zunimmt, dementsprechend der K -Wert mit steigender Temperatur abnimmt, während der zweite bedingt, dass $\frac{d\sigma}{dT}$ mit steigender Temperatur abnimmt, dementsprechend der K -Wert gleichzeitig zunimmt.

Nun stellt $\sigma\Omega$ die freie molare Oberflächenenergie dar. Bezeichnet man mit U die gesamte molare Oberflächenenergie, so gilt die thermodynamische Beziehung :

$$U = \sigma\Omega - T \frac{d\sigma}{dT} \Omega, \quad (17)$$

und für die Flächeneinheit :

$$u = \sigma - T \frac{d\sigma}{dT}. \quad (18)$$

Differentiert man dies nach T , so bekommt man :

$$\frac{du}{dT} = -T \frac{d^2\sigma}{dT^2}. \quad (19)$$

Aus Gleichung (18) lässt sich auch folgern :⁽⁶⁰⁾

$$\frac{dc_v}{d\omega} = -T \frac{d^2\sigma}{dT^2}, \quad (20)$$

wo c_v die spezifische Wärme der Flüssigkeit bei konstantem Volum bedeutet. Kombiniert man diese Beziehungen (19), (20) mit den Bedingungen (15), (16), so werden :

$$1) \quad \varphi''(r) > 0, \quad \frac{d^2\sigma}{dT^2} > 0, \quad \frac{du}{dT}, \quad \frac{dc_v}{d\omega} < 0,$$

K nimmt mit der Temperatur ab.

$$2) \quad \varphi''(r) < 0, \quad \frac{d^2\sigma}{dT^2} < 0, \quad \frac{du}{dT}, \quad \frac{dc_v}{d\omega} > 0,$$

K nimmt mit der Temperatur zu.

Hochmolekulare Verbindungen wie z. B. Triolein, Tripalmitin gehören zu dem ersten Fall, während Ameisensäure, Wasser, Phenol und andere zu dem zweiten Fall gehören.

(60) Dupré, *Ann. chim. phys.*, (4), **11** (1867), 200.

Je nachdem der K -Wert mit steigender Temperatur zunimmt oder abnimmt, verläuft die σ, T -Kurve konkav oder konvex nach der T -Achse. Fig. 7 zeigt eine schematische σ, T -Kurve, eine solche wird in der Tat von Stoff zu Stoff gefunden werden.

Bei hohen Temperaturen würden in den meisten Fällen zwischen Molekülen abstossende Kräfte hervorkommen ($\varphi(r) < 0$), und wenn in der Nähe der kritischen Temperatur die Bedingung:

$$|\varphi(r)| = n^{\frac{2}{3}} k (\vartheta_0 - T),$$

infolgedessen:

$$\frac{d\sigma}{dT} = -n^{\frac{2}{3}} k - \varphi'(r) = -n^{\frac{2}{3}} k + n^{\frac{2}{3}} k = 0$$

gilt, so wird die σ, T -Kurve sich asymptotisch der T -Achse nähern bis sie schliesslich auf die T -Achse fällt, wo

$$\sigma = 0, \quad K = 0 \quad \text{und} \quad \frac{d\sigma}{dT} = 0 \quad \text{ist.}$$

(Siehe Fig. 7.)

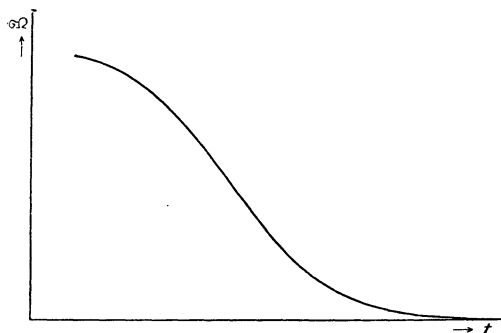


Fig. 7.

3. Über das abnorme Verhalten der anisotropen Flüssigkeiten.

Bei gewöhnlichen Flüssigkeiten kann K -Wert keineswegs negativ sein, denn, wenn er negativ wäre, so würde σ in Gleichung (9) negativ ausfallen, sofern $T < \vartheta_0$ ist, was aber allerdings unrealisierbar ist. Dagegen kann der K -Wert bei anisotropen Flüssigkeiten⁽⁶¹⁾ (eventuell bei geschmolzenen Metallen, insbesondere Cadmium⁽⁶²⁾) negativ ausfallen d. h. die Oberflächenspannung dieser Stoffe steigt mit der zunehmenden Temperatur an, im schmalen Temperaturbereich, wo sich die Flüssigkeit von anisotrop zu isotrop umwandelt. Eine derartige Ansteigung der σ, T -Kurve findet man tatsächlich in Fig. (8), (9), (10) und (11) (gezeichnet nach den Versuchen von Jaeger).⁽⁶¹⁾ Überdies sieht man dort den ganzen Verlauf der σ, T -Kurve,

(61) Jaeger, *Z. anorg. allg. Chem.*, **101** (1917), 1.

(62) Bircumshow, *Phil. Mag.*, (7), **3** (1927), 1291.

der uns viel Charakteristisches zeigt. Wie dies zustandekommt, soll unten erläutert werden.

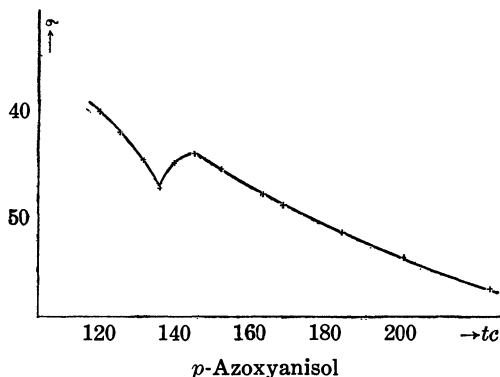


Fig. 8.

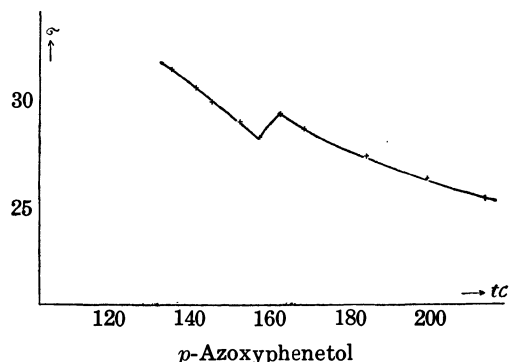


Fig. 9.

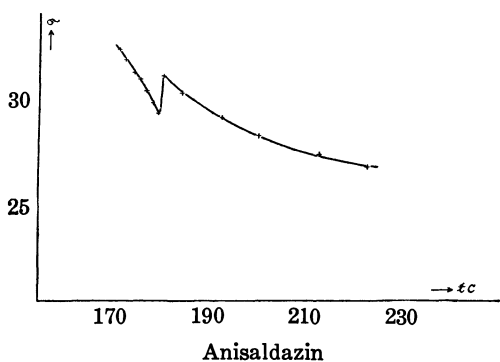


Fig. 10.

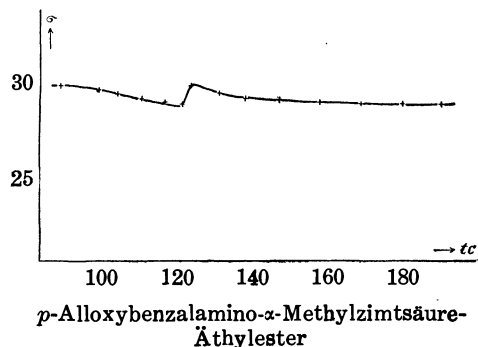


Fig. 11.

Auch für die Oberflächenschicht der anisotropen Flüssigkeiten stelle ich die zweidimensionale Zustandsgleichung auf, und zwar in die Form :

$$\sigma\Omega = N^{\frac{2}{3}}k(\vartheta^* - T) + \phi(r), \quad (21)$$

wo ϑ^* nicht mehr die kritische Temperatur, sondern die Umwandlungstemperatur (anisotrop $\rightleftharpoons$ isotrop) darstellt. Nun wird die Oberflächenspannung der anisotropen Flüssigkeiten bei $T = \vartheta^*$ nicht gleich null, und so folgt aus Gleichung (21) für $T = \vartheta^*$:

$$\sigma^*\Omega = \phi^*(r), \quad (22)$$

oder für die Flächeneinheit :

$$\sigma^* = \varphi^*(r) , \quad (23)$$

wo * den Wert beim Umwandlungspunkt charakterisiert. Diese Beziehung besagt: Die Oberflächenspannung ist bei dem Umwandlungspunkt gleich dem temperaturabhängigen Bestandteil der Kohäsionsenergie (pro Flächeneinheit).

Im Umwandlungspunkt steht die anisotrope Flüssigkeit mit der isotropen Flüssigkeit im Gleichgewicht, die letztere aber hätte ein grösseres inneres Potential als die vorige. Also würde gelten:

$$\varphi^{**}(r) > \varphi^*(r) , \quad \text{oder} \quad \sigma^{**} > \sigma^* ,$$

wo $\varphi^{**}(r)$ die Kohäsionsenergie und σ^{**} die Oberflächenspannung der isotropen Flüssigkeit, die mit der anisotropen im Gleichgewicht steht, bedeutet. Die grössere Oberflächenspannung der isotropen Flüssigkeit könnte ja nach der Schwärmetheorie von Ornstein und Kast⁽⁶³⁾ erwartet werden, da die orientierten Schwärme bei der Umwandlung (anisotrop $\rightarrow$ isotrop) abgebaut werden, indem die ungesättigten aktiven Gruppen im Molekül an der Oberfläche entblösst werden und daraus die Vermehrung der Oberflächenspannung resultiert.

Tatsächlich tritt aber die Umwandlung meist nicht ganz scharf in einem Punkt ein, sondern in einem kleinen Bereich der Temperatur, dementsprechend steigt die Oberflächenspannung ziemlich steil von einem minimalen Wert zu einem maximalen an (Fig. 8-11), während sich die Flüssigkeit von anisotrop zu isotrop umwandelt. Sobald die Flüssigkeit isotrop ist, nimmt die Oberflächenspannung, wie bei gewöhnlichen Flüssigkeiten, mit steigender Temperatur allmählich ab.

Charakteristisch ist die ganze Gestalt der σ , T -Kurve der flüssigen Kristalle. Die σ , T -Kurve verläuft anfänglich konkav nach T -Achse (der K -Wert nimmt mit steigender Temperatur zu) und beim Umwandlungspunkt steigt die σ , T -Kurve senkrecht zur T -Achse an (der K -Wert wird dabei unendlich gross) und dann, wenn die Flüssigkeit isotrop ist, verläuft die Kurve konvex nach der T -Achse (der K -Wert nimmt mit steigender Temperatur ab.). Fig. 12 zeigt einen solchen idealen Verlauf, während Fig. 8-11 den wirklichen Verlauf bei *p*-Azoxyanisol, *p*-Azoxyphenetol, Anisaldazin und *p*-Alloxybenzalamino- α -Methylzimtsäure-Äthylester zeigen.

Wenn die Beziehung:

$$\sigma^* = \varphi^*(r)$$

(63) Ornstein u. Kast, *Trans. Faraday Soc.*, **29** (1933), 931.

gültig ist, so wird die Kohäsionsenergie beim Umwandlungspunkt aus Daten der Oberflächenspannung berechnet werden. Man betrachtet hier insbesondere *p*-Azoxyanisol und *p*-Azoxyphenetol, deren langgestreckte Moleküle um eine in der Mitte befindliche polare Gruppe symmetrisch gebaut sind. Diese Moleküle haben wahrscheinlich in der smektischen Mesophase eine solche Anordnung etwa nach dem Schema wie Fig. 13 zeigt (nach Ebert und

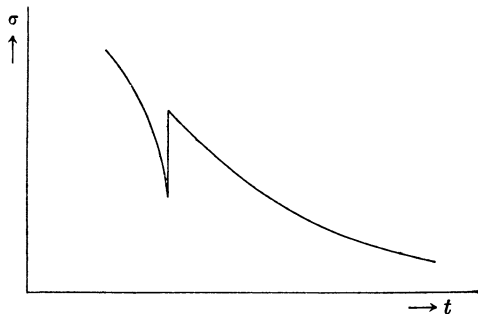


Fig. 12.

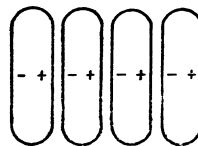


Fig. 13.

v. Hartel⁽⁶⁴⁾), indem der Vektor des elektrischen Dipolmomentes von Molekülen parallel der ausgezeichneten Achse liegt, so dass sich die entgegengesetzt geladenen Pole entsprechend aneinander hängen können.

Wenn man hier die richtenden Molekularkräfte in erster Annäherung auf die statischen Dipolkräfte zurückführen könnte, so würde folgende Beziehung entstehen :

$$\phi^*(r) = -N^{\frac{2}{3}}kT\frac{B}{\Omega} = \frac{N^{\frac{4}{3}}\pi}{2\Omega}\int_{r_0}^{\infty}r^2\frac{\partial E}{\partial r}e^{-\frac{E}{kT}}dr.$$

Setzt man hierfür

$$E = \frac{2\mu^2}{r^3}$$

ein, so wird :

$$\phi^*(r) = -\frac{N^{\frac{4}{3}}\pi}{2\Omega}\int_{r_0}^{\infty}r^2\frac{6\mu^2}{r^4} = -\frac{3N^{\frac{4}{3}}\pi\mu^2}{\Omega}\int_{r_0}^{\infty}\frac{1}{r^2}dr = \frac{3N^{\frac{4}{3}}\pi\mu^2}{\Omega r_0},$$

wo r_0 den kleinsten Abstand der Dipolzentren bedeutet. Dies in Beziehung (22) eingesetzt, ergibt :

$$\sigma^*\Omega = \frac{3N^{\frac{4}{3}}\pi\mu^2}{\Omega r_0},$$

oder

(64) Ebert u. v. Hartel, *Physik. Z.*, **23** (1927), 786.

$$\mu^2 = \frac{\sigma^* \Omega^2 r_0}{3\pi N^{\frac{4}{3}}} = \frac{\sigma^* r_0}{3\pi} \left(\frac{M}{\rho N} \right)^{\frac{4}{3}},$$

wo M das Molargewicht und ρ die Dichte bedeutet. Hier sind M , σ und ρ bekannt, somit, wenn man für r_0 einen wahrscheinlichen Wert annimmt, wird das Dipolmoment μ daraus berechnet werden.

Für p -Azoxyanisol :

$$M = 258, \quad \vartheta^*(C) = 129.5^\circ, \quad \sigma^* = 36.4 \text{ Dyn/cm},$$

$$\rho = 1.159, \quad r_0 = 4 \times 10^{-8} \text{ cm} : \quad \mu_{\text{ber.}} = 2.28 \times 10^{-18} \text{ E.S.E.}$$

Für p -Azoxyphenetol :

$$M = 286, \quad \vartheta^*(C) = 164^\circ, \quad \sigma^* = 28.3 \text{ Dyn/cm},$$

$$\rho = 1.07, \quad r_0 = 4 \times 10^{-8} \text{ cm} : \quad \mu_{\text{ber.}} = 2.26 \times 10^{-18} \text{ E.S.E.}$$

Die Dipolmomente dieser Substanzen wurden von Ebert und v. Hartel⁽⁶⁵⁾ dielektrisch gemessen: $\mu = 2.3 \times 10^{-18}$ für p -Azoxyanisol, $\mu = 2.24 \times 10^{-18}$ für p -Azoxyphenetol. Die berechneten Dipolmomente stehen also mit den beobachteten Dipolmomenten in vorzüglicher Übereinstimmung.

Die Bornsche Theorie⁽⁶⁶⁾ der flüssigen Kristalle ist von Ebert und v. Hartel kritisiert worden. Über die Verwendbarkeit der Bornschen Betrachtungen über die flüssigen Kristalle auf die orientierten Oberflächenschichten habe ich im Anschluss an die Jungsche Arbeit⁽⁶⁷⁾ schon in meiner vorhergehenden Bericht kurz diskutiert.⁽⁶⁸⁾

Zusammenfassung.

Im Hinblick auf die grosse Bedeutung der Grenzflächenerscheinungen ist es wünschenswert eine allgemeine Theorie und eine Systematik zu geben. Dies ist uns zum mindesten für die Grenzfläche flüssig-gasförmig gelungen, sei es die Oberflächenschicht reiner Flüssigkeiten oder die adsorbierte Schicht, indem man für die Schicht unter besonderer Berücksichtigung der Zwischenmolekularkräfte eine allgemeine zweidimensionale Zustandsgleichung aufstellt.

(65) Ebert u. v. Hartel, loc. cit.

(66) Born, *Ann. Physik*, **55** (1918), 222.

(67) Jung, loc. cit.

(68) Tamamushi, *Dieses Bulletin*, **6** (1931), 207.

1. Die Zustandsgleichung der adsorbierten Schicht wurde mittels der Virial-Methode abgeleitet.

2. Mit Hilfe der Zustandsgleichung der adsorbierten Schicht wurden Adsorptionsgleichungen, insbesondere die Adsorptionsisotherme von Langmuir und diejenige von Freundlich, thermodynamisch hergeleitet.

3. Die theoretisch hergeleiteten Beziehungen wurden mit den empirischen Daten, die besonders für die homologe Reihe der normalen Fettsäuren gewonnen sind, verglichen.

4. Es wurden Überlegungen über die Natur der lateralen Kohäsionskräfte bei den Fettsäuren angestellt. Die Kohäsionskräfte wurden zum Teil dem elektrostatischen Effekt und zum anderen Teil dem quantenmechanischen Effekt zugeschrieben. Der letzt genannte Effekt erklärte das Anwachsen der Kohäsion mit der Kettenlänge der Moleküle. Es wurde auf die Rolle der lateralen Kohäsion bei der Strukturbildung der adsorbierten Schicht hingewiesen.

5. Es wurde eine Deutung der Traubeschen Regel angegeben. Dass die Traubesche Regel auch in verdichteten Schichten, wo die parallele Orientierung von Molekülen von keiner Seite angezweifelt wird, gültig ist, wurde durch solchen Mechanismus bestätigt, dass die Kohlenwasserstoffketten infolge der zwischen ihnen wirkenden Molekularkräfte aus dem Innern der Lösung zur Oberfläche um so kräftiger herausgedrängt werden, je länger sie sind.

6. Es wurde für die Oberflächenschicht reiner Flüssigkeiten die zweidimensionale Zustandsgleichung aufgestellt.

7. In dieser Zustandsgleichung wurde die Oberflächenspannung als Summe dreier Energien d. h. der rein statischen Kohäsion, der Temperaturbewegung und der temperaturabhängigen Zwischenmolekularkräfte angegeben. Die Gleichung gab also eine Definition der Oberflächenspannung. Aus derselben Gleichung wurde die Eötvössche Formel $\sigma = K(\vartheta_0 - T)$ abgeleitet, wo K nicht eine einfache Konstante, sondern eine Funktion darstellt, die im allgemeinen von Stoff zu Stoff verschieden und auch von der Temperatur abhängig sein muss. Der abnorme kleine oder grosse K -Wert, besonders bei solchen Stoffen, wo das Zustandkommen von Assoziation sowie Dissoziation unwahrscheinlich ist, wurde auf die zwischen Molekülen in verschiedenem Mass wirkenden abstossenden oder anziehenden Molekularkräfte zurückgeführt. Die Ansteigung des K -Wertes bei der Verlängerung der Kette in den Fettsäure-Molekülen wurde mit der gleichzeitigen Zunahme der Kohäsionskräfte in Zusammenhang gebracht.

8. Auf das abnorme Verhalten der anisotropen Flüssigkeiten wurde besonders eingegangen. Es wurde eine Erklärung über den charakteristischen Verlauf der σ , T -Kurve dieser Stoffe angegeben. Das Dipolmoment

von *p*-Azoxyanisol und von *p*-Azoxyphenetol wurde näherungsweise berechnet, unter der Voraussetzung, dass die Oberflächenspannung beim Umwandlungspunkt anisotrop $\rightleftharpoons$ isotrop den temperaturabhängigen Kohäsionskräften gleich ist.

Herrn Prof. Dr. M. Katayama möchte ich an dieser Stelle für die Anregungen und die Ratschläge, mit der er in zuvorkommendster Weise meine Arbeit gefördert hat, meinen verbindlichsten Dank aussprechen.

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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. VIII.
THE RELATION BETWEEN THE CATALYTIC ACTIVITY
AND THE ADSORPTION.*

By Koshiro ISHIMURA.

Received July 26th, 1934. Published November 28th, 1934.

In the previous paper⁽¹⁾ the behaviours of the chief constituents of Japanese acid earth in the catalytic action on naphthalene have been elucidated, and it has been noted that there exists the parallelism between their chemical compositions and catalytic activities. The present paper deals with the relation between their catalytic activities and adsorptive powers. The specimens of the acid earth used in the present investigation are the same as those mentioned in the previous paper and their general descriptions are here omitted.

The adsorptive power of the acid earth greatly depends upon the nature of adsorbates, i. e. upon their acidities or basicities, and therefore the catalytic activity on naphthalene was compared with adsorptive powers for neutral substances such as water, benzene, and naphthalene itself.

From the experiments described below on the adsorption of the various specimens of the acid earth for these neutral substances, it is concluded that the larger the surface area the greater is the catalytic activity. Therefore,

* An epitomized translation of the original published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue and Ishimura, This Bulletin, 9 (1934), 431.

if the catalysis does not take place on the whole surface uniformly but only on some particular parts, the active centres, then the distribution of these active centres on the surface is approximately equal for the various specimens of the acid earth, that is, the magnitude of the catalytic activity depends upon the surface area possessing active centres equally distributed but not on the number of the active centres on the equal surface area. On the other hand, the catalytic activity is closely connected with the chemical composition, as stated in the previous paper, so it may not be illogical to consider that the surface area is influenced by the chemical composition; the larger the ratio $\text{Al}_2\text{O}_3/\text{SiO}_2$ and the smaller the ratio $\text{CaO} + \text{K}_2\text{O}/\text{SiO}_2$, the greater is the surface area.

The Adsorption of Water. Six specimens of the earth were taken. Each of them was dried at 120° , powdered, and particles with mesh-size of 60-80 were sifted out, about 0.5 g. of which were taken into the weighing

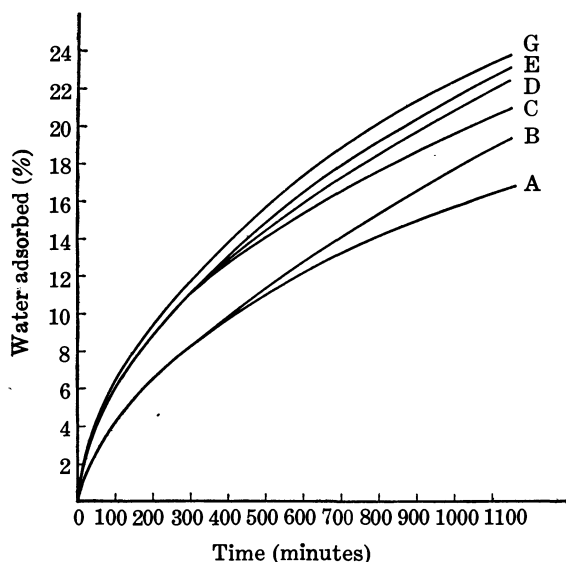


Fig. 1.

bottle, and heated at 300° in an electric furnace to a constant weight. The bottle was then put on a glass stand placed in a wide-necked bottle containing some distilled water in a thermostat of 25° . It was taken out at intervals and weighed. The amount of adsorbed water is plotted against time in Fig. 1. The letters assigned to the samples denote their order of the magnitude of the catalytic activity, earth A having the smallest activity and earth G the greatest as noted in the previous paper. Fig. 1 shows that a parallelism holds between the catalytic

activity and both the adsorption velocity and capacity up to about 20 per cent. of water adsorbed.

Adsorption velocity depends upon both the surface area and adsorption intensity, and so if adsorption intensity is constant the surface area only influences the velocity. The adsorption intensities of the acid earths for water may be taken constant after the whole surfaces are covered with several

layers of water molecules. Since the amount of water sufficient to cover the whole surface of the earth in a monomolecular layer is about 2.5 per cent. of the weight of the dry earth, as will be shown in later communications, the adsorption intensities of the various specimens of the earth may be safely taken as constant after the amount of water several times as great as the above value has been adsorbed. However, the monomolecular film of water is not necessarily formed on the whole surface before the formation of any polymolecular layer begins⁽²⁾ and, moreover, it cannot be admitted that layer adsorption only takes place all over the surface before there occurs capillary condensation even in the early stage of the adsorption under the experimental condition above mentioned. Yet if it is assumed that the distribution of radii of pores is of approximately the same probability for all specimens of the acid earth, then the adsorbed amount within certain limits can be regarded as collected on the surface by layer condensation only with a constant intensity, and therefore their adsorption velocities for water depend upon the surface areas only and the adsorbed amounts within those limits can be taken as measures of the surface areas, when the various specimens of the acid earth are taken into consideration in comparison with one another. Therefore it seems that the curves given in Fig. 1 can be interpreted as showing that the larger the surface area the greater is the catalytic activity.

The Adsorption of Benzene. The integral heats of wetting of the various specimens of the acid earth in benzene were compared by the method proposed by Berl and Andress⁽³⁾ who have shown that the integral heats of wetting of porous materials such as active charcoals and silica gels can be taken as measures of their adsorptive powers and that ether isotherms for various charcoals are practically quantitatively related to the heats of wetting in benzene. The apparatus and manipulation were practically the same as those of Berl and Andress. The double wall was formed with two test-tubes of different sizes and a rubber stopper, and pure benzene (d_4^{25} , 0.8731) (10 c.c.) was poured into the inner tube fitted with a thermometer graduated to 0.1° . After the temperature became constant for about 5 minutes, the earth (sifted by a 200 mesh sieve and dried at 300° for one hour) (3.00 g.) was weighed out and rapidly put into the benzene, the thermometer being lifted meanwhile, and then serving as a stirrer. The change of temperature was recorded at the interval of one minute to 0.01° . In every case

(2) In fact, the experiments to be described in the next communication seem to indicate that there remain some parts uncovered on the surface even in the neighbourhood of saturation.

(3) *Z. angew. Chem.*, **35** (1922), 722;

the mercury thread climbed to a maximum position within one minute and then gradually fell down. The sum of the rise and fall at the ends of the first two minutes was taken as a measure of the heat of wetting as proposed by the German authors. It is necessary to start each experiment at temperature not so different in order to keep all such heat measurements comparable. The results are shown in Table 1.

Table 1.

Earths	Temperature changes	Means	Yields of resinous matter (g.)
A	$\begin{cases} 0.84 \\ 0.89 \end{cases}$	0.87	1.65
B	$\begin{cases} 1.53 \\ 1.57 \end{cases}$	1.55	1.82
C	$\begin{cases} 1.71 \\ 1.74 \end{cases}$	1.73	1.86
D	$\begin{cases} 1.71 \\ 1.93 \end{cases}$	1.82	1.90
E	$\begin{cases} 2.38 \\ 2.19 \end{cases}$	2.29	2.10
F	$\begin{cases} 2.63 \\ 2.66 \end{cases}$	2.65	2.23
G	$\begin{cases} 2.87 \\ 2.59 \end{cases}$	2.73	2.60

In the fourth column, the catalytic activities on naphthalene measured by the yields of resinous matter are cited from the previous paper.⁽⁴⁾

The above results are quite analogous to those shown in Fig. 1; the catalytic activity goes parallel with the heat of wetting.

The heat evolved when solid is wetted by liquid is due to some surface phenomenon, but it is hardly conceivable that when liquid is stored in large pores it would give rise to the heat effect of measurable magnitude, hence the heat of wetting may be a function of both the intensity and capacity factors of adsorption,—whether it

is the layer adsorption or the condensation in capillaries of molecular size or both—but not a function of the saturation capacity. A number of papers⁽⁶⁾ have been published which show that the heat of wetting is a function of the surface area. It seems, however, that there must be an implied assumption that the surface is homogeneous or if heterogeneous there is no appreciable difference in the heat effect between the active and inactive parts⁽⁶⁾ or, if any, it is negligible compared with the total heat evolved. The catalytically active parts on the surface of solid catalysts represent generally very small fraction of the total surface area⁽⁷⁾ and

(4) Loc. cit.

(5) Macy, *J. Phys. Chem.*, **34** (1931), 1397; Berl and Burkhardt, *Z. angew. Chem.*, **43** (1930), 332; Bartell and Fu, *Colloid Symposium Annual*, **7**, 135.

(6) Lamb and Coolidge found that the heats of adsorption of vapours are very nearly equal on inactive as on active charcoals of the same kind (*J. Am. Chem. Soc.*, **42** (1920), 1146).

(7) Rideal and Wright, *J. Chem. Soc.*, **127** (1925), 1352; Hoover and Rideal, *J. Am. Chem. Soc.*, **49** (1927), 122; Garner, Mckie and Knight, *J. Phys. Chem.*, **31** (1927), 644.

therefore even if the heat evolved on the adsorption of molecules directly held on these particular parts be much greater than on other parts or than of molecules localized on the upper parts of the adsorbed layers, their effect may be very small compared with the total heat quantity. Therefore the heat of wetting in general may be taken as an approximate measure of the surface area for the same kind of catalysts.

Thus the same conclusion may be attained from Table 1 that the larger the surface area the greater is the catalytic activity of the acid earth.

The values of the heat of wetting fall considerably as the drying temperature of the acid earth is raised. The temperature change due to the heat of wetting measured by the above-mentioned method is plotted against the drying temperature of earth F in Fig. 2. Each sample was dried at the required temperature for one hour. There may occur the sintering of catalyst mass causing the diminution of the surface area as temperature rises, yet at the same time more severe change of the surface may take place with the liberation of water, the nature of the acid earth thereby suffering the fundamental change as believed by many authors.⁽⁸⁾

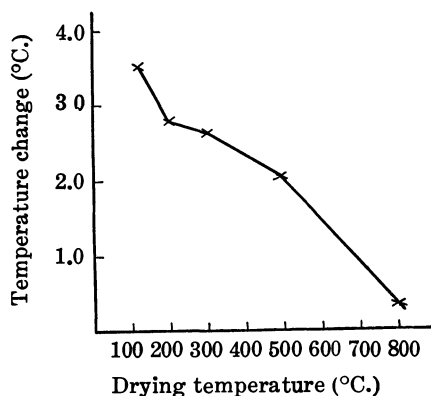


Fig. 2.

The heats of wetting of various materials other than the acid earth were compared by the same method. All of the samples are the same as those described in the previous paper.⁽⁹⁾ The data are tabulated in Table 2,⁽¹⁰⁾ in which the catalytic activities are also quoted from the previous paper.

It would be impossible to compare the surface areas of these substances of widely different natures by the heats of wetting, because their adsorption intensities for benzene would be greatly different from one another, though it is noticed that such substances as active charcoal and silica gel generally accepted as of very large surface areas evolve the larger heat quantities. There can be denoted no relationship between the heat of wetting and the catalytic activity given in Table 2.

(8) Kobayashi, Yamamoto and Bito, *J. Soc. Chem. Ind. Japan*, **32** (1929), 298B; Kameyama and Oka, *ibid.*, **32** (1929), 94B; Isobe, *Sci. Papers of Inst. Phys. Chem. Research, Japan*, **14** (1930), 229.

(9) Loc. cit.

(10) In case of voluminous substances such as active charcoal and diatomaceous earth 1.5 g. were taken and the observed values of the temperature change were doubled.

Table 2.

Subst.	Earth F	Earth F treated with HCl	Bentonite	Bentonite treated with HCl	Caoline	Clay I	Diatom. earth	Bauxite	Active charcoal	Silica gel a	Al(OH) ₃ b
Temp. Change	2.65	3.18	2.93	2.11	0.45	1.02	0.91	5.13	6.80	6.60	4.57
Yields of resinous matter	2.23	2.33	0.25	2.89	0.81	0.33	0.22	0	0	0.03	0.02

As for bentonite, the surface area suffers little change by the treatment with hydrochloric acid, while its catalytic activity is increased greatly owing to the removal of poisons from the surface as suggested in the previous publication. In the case of the acid earth, its chemical composition and consequently its catalytic activity as well as its surface area is increased by a small degree by the same treatment.

The Adsorption of Naphthalene. Naphthalene has a very small vapour pressure at ordinary temperature and it will take a very long time for it to saturate adsorbents, while the complication of the apparatus and the difficulty of manipulation would be accompanied in experiments at high temperatures. A rigorous temperature regulation is not needed in the present experiment, since what is required is not the correctness of values but only relative adsorptive powers. So the experiment was carried out at room-temperature as follows. About 0.5 g. of each acid earth (sifted by a 200 mesh sieve and dried at 300° for one hour) is weighed in a weighing bottle of the same size, put in a desiccator of sulphuric acid ($d = 1.84$), and left to stand for 7 days, and then a dish containing naphthalene, dried beforehand on sulphuric acid of the same specific gravity, is placed at the centre of the desiccator. Naphthalene is slowly adsorbed by the earth. The weighing bottle is taken out at intervals and weighed. The amount adsorbed is plotted against time as shown in Fig. 3. The increase or decrease in the weight of the earth due to the difference between the vapour pressure of the acid earth and that of sulphuric acid is negligible as a blank test has shown.

The magnitude of the surface area of the acid earth is of the order of about 10 square metres per gram as will be shown in later communication and it is very probable that the adsorbed naphthalene forms a monomolecular

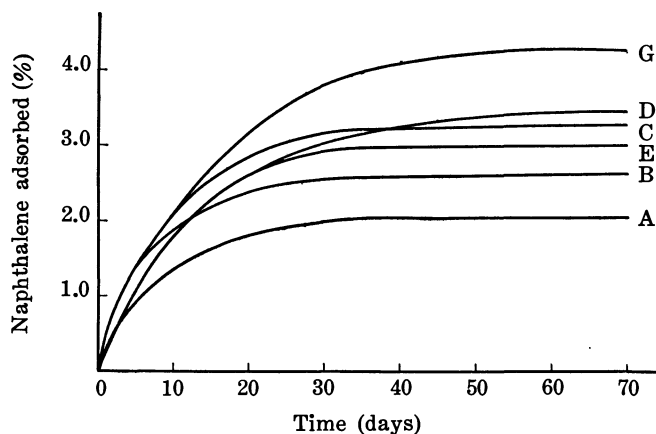


Fig. 3.

film on the surface,⁽¹¹⁾ if its molecular dimensions and the amounts adsorbed by the acid earths are taken into consideration.⁽¹²⁾ Therefore, the surface areas of the earths may be roughly measured by the saturation capacities for naphthalene. Fig. 3 shows that the surface area goes parallel with the catalytic activity (with one exception of the earth designated E). Thus the author has come here again to the same conclusion.

As has been stated in the previous paper, the catalytic activity is almost entirely destroyed by the addition of about 3 per cent. of sodium hydroxide or lime. The surface area and consequently the amount of adsorbed naphthalene, however, will not change greatly as long as pores are not blocked up by the added matter. If, on the contrary, the amount added is large enough to block up some of small pores, then the diminution of the surface will occur, manifested by the decrease in the amount of adsorbed naphthalene. Plots given in Figs. 4 and 5 are in close agreement with the above speculation. There are three breaks in every curve, which seems to be unavoidable under the experimental condition mentioned above, since the temperature of the laboratory and the vapour pressure of naphthalene rose gradually as the experiment extended from the 8th of December, 1930, to the 4th of April, 1931.

(11) It is improbable, however, that a perfect monomolecular film is always formed, for in the course of the adsorption of naphthalene the colour of the earths turns gradually from light yellow to brownish black, indicating that at room temperature there occurs already the catalytic action.

(12) The dimensions of naphthalene molecule are 8.68 by 6-7 by 3×10^{-8} cm. (Adam, *The Physics and Chemistry of Surfaces*, 1930, p. 95). A calculation shows that the area to be covered by 0.02 g. of naphthalene is 17.0-58.8 square metres according to the orientation of the molecules on the assumption of a packed monomolecular layer.

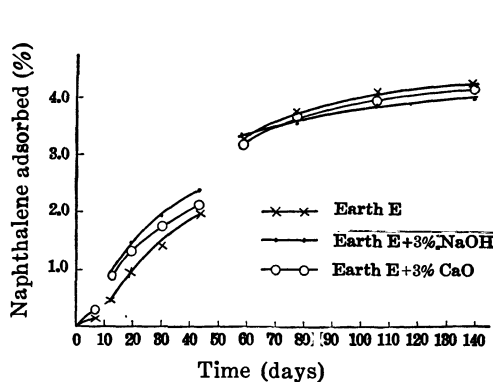


Fig. 4.

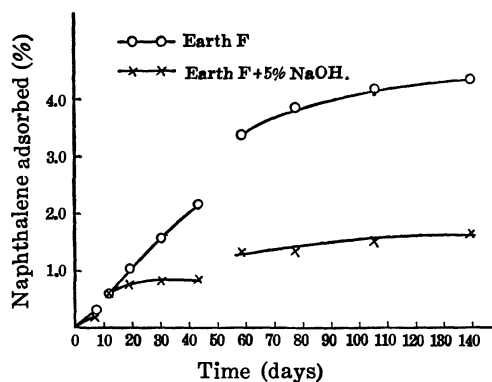


Fig. 5.

Fig. 6 shows the curves of the adsorbed amount plotted against time for several substances together with that for earth F. The substances are the same as those given in Table 2. The amount adsorbed by active charcoal is about ten times as great as that by the earth, and the surface of the

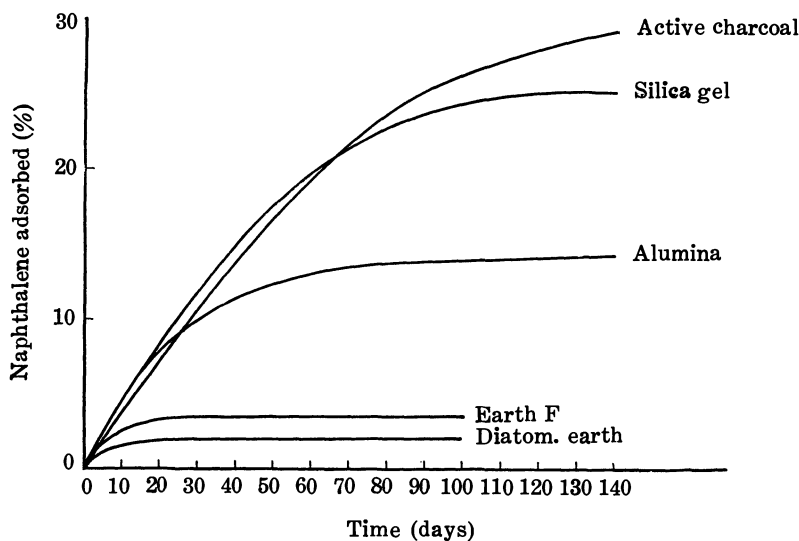


Fig. 6.

former is also about ten times as large as that of the latter, as will be shown in later paper. It is very probable therefore that the surface areas of several materials of widely different natures also can be compared with one another by the saturation capacities for naphthalene. A close parallelism is observed also between the data given in Table 2 and Fig. 6.

Summary.

(1) The catalytic activity of Japanese acid earth on naphthalene has been compared with its adsorptive powers for water, benzene, and naphthalene.

(2) The relations between the adsorptive powers and the surface area of the earth have been discussed.

(3) It has been concluded that the larger the surface area the greater is the catalytic activity and therefore the magnitude of the catalytic activity depends upon the surface area possessing active centres equally distributed but not on the number of the active centres on the equal surface area.

(4) The influence of the chemical composition of the earth on its surface area has been suggested.

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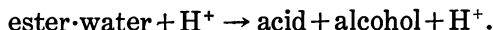
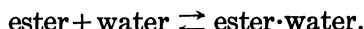
ON THE VAPOUR-PHASE HYDROLYSIS.

By Shigeaki YAMASAKI and Toshizo TITANI.

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There have been a great many investigations on the reactions of organic compounds with water, particularly in connection with the hydrolysis of esters in aqueous solutions. All these results have brought about a number of theories regarding the mechanism of the reaction: the theory generally accepted states that the hydrolytic reaction occurs in two stages, the first being a rapid formation of a substrate-water complex and the second the subsequent reaction of the complex with hydrogen-ion to give final products of the hydrolysis.⁽¹⁾ For example, the hydrolysis of esters in aqueous solutions can be represented by the following scheme :

(1) Cf., for example, F.O. Rice, "The mechanism of homogeneous organic reactions," Chemical Catalog Co., 1928, 104.



If the above-mentioned mechanism be correct, then the hydrolytic reaction should be very difficult to occur in the vapour phase, where the formation of the substrate-water complex will be greatly retarded and at the same time ions are not known to exist at least in the stable form. As there have been very few works on the reactions of organic compounds with water vapour, it occurred to the present authors that an inquiry into the nature of this type of reactions in the vapour phase would be interesting. Although Berthelot and Péan de St. Gilles⁽²⁾ already noticed in their

memorial work on the ester equilibrium that not only the formation but also the hydrolytic decomposition of ethyl acetate was greatly retarded in the vapour phase, and G. Harker⁽³⁾ has recently pointed out that benzyl chloride is slowly attacked by liquid water but not by steam.

The present paper is concerned with the non-reactivity of water vapour on benzyl chloride, the reaction of which with liquid water was already studied by one of the authors a few years ago,⁽⁴⁾ and on ethyl acetate, which is one of the typical substances for the study of the hydrolytic reaction.

The reaction vessel shown in Fig. 1 is made of glass and has half a liter capacity. It was well cleaned with chromic mixture and steamed before every use. Weighed quantities of the ester and water were separately sealed in small thin-walled glass bottles of about 0.1 c.c. capacity. The ester-bottle was placed on the bottom of the center tube B and the water-bottle on the bottom of the tube C. A glass rod a few centimeters long was placed over each bottle, and both tubes B and C were connected by fusing at points D with respective side tubes in the lower part of the reaction vessel. The reaction vessel was then well pumped out through tube A and was sealed off at point A. After the small bottles containing substances were

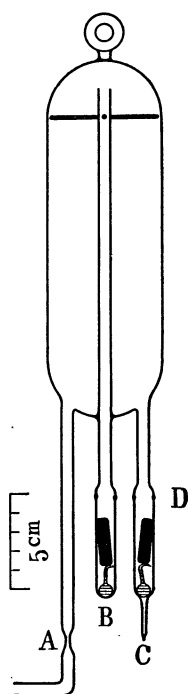


Fig. 1.
Reaction Vessel

(2) Berthelot and Péan de St. Gilles, *Ann. chim. phys.*, **65** (1865), 385; *Chem. Z.*, **7** (1862), 908.

(3) G. Harker, *J. Chem. Soc.*, **1924**, 500.

(4) T. Titani and K. Kurano, *Bull. Chem. Soc. Japan*, **6** (1931), 152.

broken by hammering them with the glass rods (caused by shaking), the reaction vessel was placed in an electrically heated air thermostat. The temperature was gradually raised up to the desired point, where it was able to be maintained constant automatically within $\pm 1^\circ$ for a long period. The quantities of the substances taken are shown in Table 1, where the total pressure exerted by the vaporized substances in the reaction vessel was calculated.

Table 1. Average amounts of the substances taken.

Substance	Temp. C.	Ester in mol	Water in mol	Total pressure calc. in atm.
Benzyl chloride	130°	0.0005	0.0004	0.06
	200°	0.001	0.005	0.30
Ethyl acetate	130°	0.001	0.001	0.13
	200°	0.002	0.008	0.78

After the reaction vessel was heated for a measured time, it was taken out of the thermostat and was quickly cooled down. As soon as it attained room temperature, a measured quantity of water (about 30 c.c. twice) was forced into the vessel through the right side tube C by breaking its capillary end in the water. The reaction vessel was rinsed in this way and whole water thus employed was carefully collected to be titrated against 0.02 N baryta, the titration being carried out as soon as possible. A few drops of the baryta were found enough, in most cases, to give an end point. A slight correction due to the carbonic acid from air had to be taken into consideration. The acidity thus determined was divided by the total mols of the ester employed, and then multiplied by 100. This value, which may be regarded as a percentage decomposition of the ester, is plotted against the duration of each run in hours (small circles in Fig. 2 and 3). Small triangles in these figures represent the results of the comparative experiments where the vapour of ester only was heated without an addition of water vapour. It will be seen from the figures that the degree of decomposition is very small in every case, on the whole 0.5% for benzyl chloride at 130°C. and 200°C. and 0.05% for ethyl acetate at 200°C. No trace of decomposition was found for ethyl acetate at 130°C. even after 150 hours' heating. This slight tendency to decompose is, moreover, always the same

irrespective of whether the esters are heated with or without an addition of water vapour. This slight decomposition is by no means caused by the hydrolytic reaction in vapour phase, but either by the hydrolysis in the

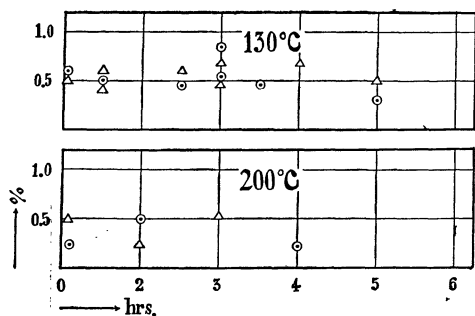


Fig. 2. Benzyl chloride

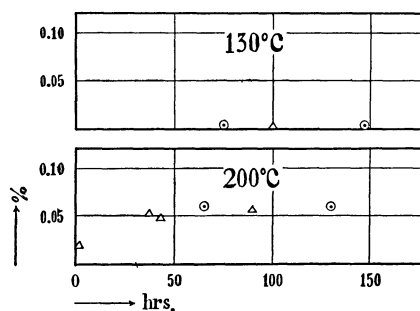


Fig. 3. Ethyl acetate

liquid phase during the washing and titration or by the thermal decomposition in the vapour phase. It was tried to avoid as far as possible the thermal decomposition at the temperatures employed by keeping the inner surface of the vessel clean and by gradually raising the temperature of the thermostat, so as not to superheat the esters in the liquid state. Nevertheless, the thermal effect became too remarkable at 300°C. to obtain a reproducible result above this temperature.

We may draw a following conclusion from the result so far obtained : (1) the hydrolysis is not a merely molecular reaction between ester and water molecules ; (2) the heat of activation for the hydrolytic reaction in the vapour phase will be much larger than that of the thermal decomposition or polymerization.

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HETEROGENEOUS CHEMICAL REACTIONS IN THE
SILENT ELECTRIC DISCHARGE. XI.

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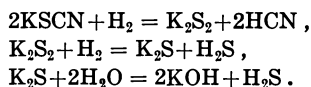
The results of investigations obtained since the publication of the previous papers⁽¹⁾ are described in this paper. The apparatus and the procedure of the experiments are essentially the same as mentioned previously.

(1) **Potassium Thiocyanate.** Exp. 1. The quantity of potassium thiocyanate KSCN employed = 7.0 g. Time of silent electric discharge = 7 hours. On leaving the discharge tube the gas was passed first through distilled water and then through an alkaline solution.

The solid reaction product was dissolved in water, when a light yellow solution with the following properties was obtained. (1) It was alkaline. (2) The presence of sulphide was proved by means of sodium nitroprusside.⁽²⁾ By analyzing the distilled water, through which the gaseous reaction product had been passed, the formation of hydrogen cyanide and hydrogen sulphide during the discharge was proved exactly as in the case of mercuric thiocyanate.⁽³⁾

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of potassium thiocyanate employed = 7.00 g. Time of silent electric discharge = 5 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 4.50 c.c.

From these experimental results it seems that the principal reactions in the discharge tube are expressed by the following equations, the reaction products being potassium hydroxide, potassium sulphide, hydrogen sulphide, and hydrogen cyanide.



(2) **Potassium Silver Cyanide.** Exp. 1. The quantity of potassium silver cyanide $\text{KAg}(\text{CN})_2$ employed = 7.0 g. Time of silent electric

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320.

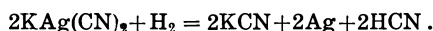
(2) Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 13th Ed., Vol. 1, p. 391.

(3) S. Miyamoto, this Bulletin, **9** (1934), 177.

discharge = 5 hours. Exactly as in the case of silver cyanide,⁽⁴⁾ the formation of metallic silver and hydrogen cyanide was proved.

Exp. 2. The quantity of hydrogen cyanide produced was determined exactly as in the case of silver cyanide.⁽⁴⁾ Potassium silver cyanide employed = 7.00 g. Time of silent electric discharge = 5 hours. The quantity of hydrogen cyanide produced = 0.0002 g.

From these experimental results it seems that the principal reaction in the discharge tube is expressed by

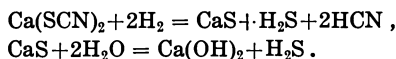


(3) **Calcium Thiocyanate.** Exp. 1. The quantity of calcium thiocyanate $Ca(SCN)_2 \cdot 3H_2O$ employed = 7.00 g. Time of silent electric discharge = 6 hours. A gas absorption bottle containing a potassium hydroxide solution was connected with the discharge tube.

The reaction product in the discharge tube was shaken with water; a yellow solution was obtained, which had the following properties. (1) It was acidic. (2) The absence of sulphide was proved by means of sodium nitroprusside. The evolution of hydrogen cyanide and hydrogen sulphide was proved by analyzing the alkaline solution, through which the gaseous reaction product had been passed on leaving the discharge tube.

Exp. 2. The quantity of hydrogen sulphide produced was determined. Calcium thiocyanate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.50 c.c.

From these experimental facts it seems that the principal reactions are expressed by the following equations:



(4) **Ammonium Thiocyanate.** Exp. 1. The quantity of ammonium thiocyanate NH_4SCN employed = 7.00 g. Time of silent electric discharge = 7 hours. On leaving the discharge tube the gas was passed first through an alkaline solution and then through dilute sulphuric acid.

On passing the electric current the powder in the discharge tube became slightly yellow. It was shaken with water and filtered. A small quantity of yellow powder remained, which is supposed to be sulphur. The filtrate was neutral and contained no appreciable quantity of sulphide. By analyzing the alkaline and sulphuric acid solutions through which the gas had been

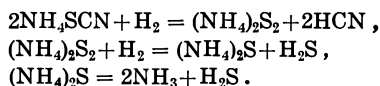
(4) S. Miyamoto, this Bulletin, **9** (1934), 178.

passed, it was proved that hydrogen sulphide, hydrogen cyanide, and ammonia gas were reaction products.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of ammonium thiocyanate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 2.00 c.c.

Exp. 3. The quantity of ammonia gas, absorbed by sulphuric acid, was determined in the usual manner.⁽⁵⁾ The quantity of ammonium thiocyanate employed = 7.00 g. Time of silent electric discharge = 7 hours. Volume of sulphuric acid solution of 0.01000 normal, equivalent to the quantity of ammonia produced = 3.02 c.c.

From these experimental facts it seems that the principal reaction products are hydrogen sulphide, hydrogen cyanide, and ammonia gas, and that the reactions in the discharge tube are expressed by the following equations:



(5) **Sodium Thiosulphate.** Exp. 1. The quantity of sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ employed = 7.00 g. Time of silent electric discharge = 8 hours. A gas absorption bottle, containing a potassium hydroxide solution, was connected with the discharge tube. On passing the electric current no appreciable change was observed in the appearance of the powder in the discharge tube. Water was added to the solid reaction product, well shaken, and filtered. A small quantity of white powder, undoubtedly sulphur, remained. The filtrate had the following properties. (1) It was alkaline. (2) The absence of sulphide was proved by means of sodium nitroprusside. (3) The presence of sulphite was proved by the method of E. Votocek.⁽⁶⁾ By analyzing the alkaline solution in the absorption bottle, it was proved that hydrogen sulphide was a reaction product.

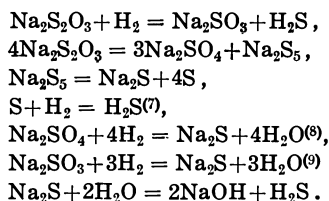
It was thus proved that the principal reaction products are sulphite, sulphur, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of sodium thiosulphate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.82 c.c.

(5) Treadwell, "Kurzes Lehrbuch der analytischen Chemie.," 10th Ed., Vol. 2, p. 483.

(6) Treadwell-Hall, "Analytical Chemistry," 8th. Ed., Vol. 1, p. 416.

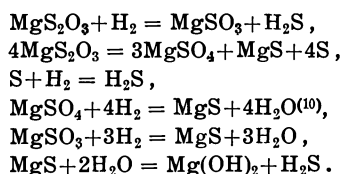
It seems that the principal reactions in the discharge tube are expressed by the following equations :



(6) **Magnesium Thiosulphate.** Exp. 1. The quantity of magnesium thiosulphate $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ employed = 7.00 g. Time of silent electric discharge = 7 hours. Exactly as in the case of sodium thiosulphate it was proved that the principal reaction products are sulphite, sulphur, and hydrogen sulphide.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of magnesium thiosulphate employed = 7.00 g. Time of silent electric discharge = 7 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 9.04 c.c.

From the results of the experiments it seems that the reactions in the discharge tube are expressed by the following equations :



(7) **Barium Thiosulphate.** Exp. 1. The quantity of barium thiosulphate BaS_2O_3 employed = 7.00 g. Time of silent electric discharge = 6 hours. No appreciable change was observed in the appearance of the powder in the discharge tube. The solid reaction product was shaken with an excess of a sodium carbonate solution and filtered. The presence of sulphide and sulphite in the filtrate was proved exactly as in the case of sodium thiosulphate. It was proved that hydrogen sulphide was contained in the gas which left the discharge tube.

(7) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 726.

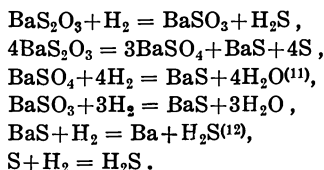
(8) *Ibid.*, **54** (1933), 86.

(9) *Ibid.*, **54** (1933), 1231.

(10) *Ibid.*, **53** (1932), 940.

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of barium thiosulphate employed = 7.00 g. Time of silent electric discharge = 6 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 1.50 c.c.

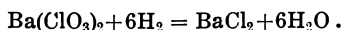
From these experimental results it seems that the reactions in the discharge tube are expressed by the following equations :



(8) **Barium Chlorate.** Exp. 1. The quantity of barium chlorate $\text{Ba}(\text{ClO}_3)_2$ employed = 7.0 g. Time of silent electric discharge = 6 hours. The formation of chloride was proved in the usual manner.

Exp. 2. The quantity of chloride produced was determined exactly as in the case of potassium chlorate.⁽¹³⁾ The quantity of barium chlorate employed = 7.00 g. Time of silent electric discharge = 6 hours. The volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of barium chloride produced = 15.10 c.c.

It was proved that the principal reaction in the discharge tube is expressed by



Summary.

The chemical reactions under the silent electric discharge were studied when hydrogen reacted with the following inorganic solid substances.

(1) Potassium thiocyanate. Reaction products: hydrogen cyanide, hydrogen sulphide, and potassium sulphide.

(2) Potassium silver cyanide. Reaction products: silver and hydrogen cyanide.

(3) Calcium thiocyanate. Reaction products: hydrogen cyanide, hydrogen sulphide, and calcium hydroxide.

(11) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 935.

(12) *Ibid.*, **53** (1932), 936.

(13) *Ibid.*, **53** (1932), 731.

(4) Ammonium thiocyanate. Reaction products: hydrogen cyanide, ammonia, and hydrogen sulphide.

(5) Sodium thiosulphate. Reaction products: sodium sulphite, hydrogen sulphide, and sulphur.

(6) Magnesium thiosulphate. Reaction products: Magnesium sulphite, hydrogen sulphide, and sulphur.

(7) Barium thiosulphate. Reaction products: Barium sulphite, barium sulphide, hydrogen sulphide, and sulphur.

(8) Barium chlorate. Reaction products: barium chloride and water.

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THE COLLOIDAL BEHAVIOUR OF SERICIN. VII.*

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Sec. V. The Distribution of the Various Forms of Nitrogen in Sericin A and Sericin B.

The very close resemblance in properties between naturally occurring proteins and the higher synthetic polypeptides suggests that proteins are essentially formed by the condensation of varying numbers of groups of diamino- and monoamino-acids mainly by means of the peptide linkage.

R. Inoue, Abderhalden, and others have thoroughly investigated the nitrogen distribution in the true and the wild silks, and R. Inoue showed that fibroin and sericin are similar in the distribution of various forms of nitrogen, but their amino-acid compositions are greatly different. In order to compare the nitrogen distribution in sericin A and sericin B I have studied the same problem.

As for the structure of proteins, the molecule is found to consist essentially of a main-axis constructed with repeated three-atom-units in a zigzag chain. The middle carbon atom of the three-atom-unit joins an organic

* Continued from p. 474 of this volume, and concluded.

radical forming a long side-chain. If the side-chain be such a group as hydrogen, methyl, $\text{CH}_2(\text{OH})-$, etc., that is, if the chain is formed of glycocoll, alanine, serine, etc., the molecule is permitted to pack together sufficiently closely to form fibers. In the case of silk fibroin, no less than 40 per cent. of the weight of the protein appears as glycocoll and a further 25 per cent. as alanine, so that most part of side-chain components in this protein is hydrogen-atom and methyl-group.

The contents of glycocoll and alanine in sericin are much less than in silk fibroin, so we can presume that in sericin molecules the main-axis components are smaller, but the side-chain components are greater than in fibroin. If a protein molecule has long, bulky side-chains, its main-axis cannot be brought into close approximation to that of another molecule of the same kind, but there will be a space left between them, and this space, in an aqueous solution, will obviously be filled up mainly with water and thus will be hydrated. The difference in the proportion of their components leads to easy separation into two proteins, fibroin and sericin, on boiling in water.

If the quantity of the nitrogen dissolved in water observed by R. Inoue and K. Kitazawa,⁽⁶⁰⁾ is compared with the lysine contents of silk, both are closely related as given in Table 105.

Table 105.

	N (%) dissolved in water by an hour boiling	Lysine content (%)
True silk	1.789	0.86
Antheraea Yamamai silk	1.339	0.19
Antheraea pernyi silk	0.428	0.03
Attacus cynthia silk	0.110	0.04

Amino-acid composition of sericin has been reported as shown in Table 106.

Table 106.

	Amino-acids	Turk ⁽⁶¹⁾	Abderhalden	Inoue
Main-axis components	Glycocoll	—	1.1	4.38
	Alanine	—	10.10	8.86
	Serine	6.81	11.25	4.45

(60) R. Inoue and K. Kitazawa, *Bull. Seri. and Silk Ind. Japan*, **5** (1932), No. 1.

(61) Turk, *Z. physiol. Chem.*, **111** (1932), 69.

Table 106. (*Concluded*)

	Amino-acids	Turk	Abderhalden	Inoue
Side-chain components	Tyrosine	—	3.50	—
	Arginine	4.56	3.75	5.67
	Lysine	1.69	1.90	3.51
	Histidine	1.02	1.00	1.99

G. Yamanouchi⁽⁶²⁾ reported that in the silk gland of silkworms fibroin is surrounded by three sericin layers which are different in the degree of dyeing with acid fuchsin. The sericin in the outer layer, S_3 , is dyed the most easily with this colour and the sericin in the middle layer, S_2 , is difficult to be dyed.

I have shown that the cocoon layer having good "kaijo" possesses a greater capacity of adsorbing dyes than that having bad "kaijo", and that sericin A can adsorb many dyes like acid fuchsin, congo red, methylviolet, etc. stronger than sericin B. From these results it seems to me that these two components of sericin is separately secreted from different parts of the silk gland.

Six grams of sericin A or sericin B was dissolved in 120 c.c. of 30 per cent. hydrochloric acid and the solution was boiled in a tared flask under a reflex condenser until it gave no longer the biuret reaction. After 6 hours the hydrolysis of sericin was stopped and the solution was filtered, and diluted to 500 c.c. Various forms of nitrogen in sericin were determined by van Slyke's method. The results are given in Table 107.

Table 107.

	Sericin A (%)	Sericin B (%)	Sericin (%) (Inoue)	Fibroin (%) (Inoue)
Amide N	2.63	2.40	2.34	1.26
Humine N	2.51	2.47	1.93	2.05
Cystine N	0.70	0.83	0.70	0.40
Arginine N	8.43	5.14	5.67	4.85
Histidine N	0.69	2.48	0.49	6.74
Lysine N	4.34	4.83	4.88	0.13
Mono-amino N	76.74	80.53	81.52	75.19
Non-amino N	2.60	2.02	2.34	7.42
Hexon base N	14.16	13.28	11.74	12.12
Lys.+arg. N	12.77	9.97	10.55	4.98

(62) G. Yamanouchi, *J. Coll. Agri. Hokkaido Imp. Univ.*, **10** (1922), Part 4, 1-41.

As shown in Table 107, sericin A and sericin B are similar in the distribution of various forms of nitrogen. Sericin A is poorer in mono-amino nitrogen and richer in non-amino and hexon base nitrogen than sericin B. This difference may lead to different physico-chemical behaviours in viscosity, swelling, and gelatinization.

Block and Vickery⁽⁶³⁾ found that the basic amino components in keratins obtained from various sources have the following proportion :

$$\text{Histidine : Lysine : Arginine} = 1 : 4 : 12.$$

The results for sericin are shown in Table 108.

Table 108.

	Histidine : Lysine : Arginine
Sericin A	0.69 : 4.34 : 8.42 = 1 : 6.3 : 12.2
Sericin B	2.48 : 4.83 : 5.14 = 1 : 1.9 : 2.7
Fibroin	(Vickery and Block) 1 : 3.6 : 10.6

The molecular weights calculated on the assumption that the molecule of sericin contains one molecular equivalent of arginine, or lysine, are shown in Table 109.

Table 109.

	Sericin A	Sericin B
Arginine	17835	—
Lysine	20423	18718

The number obtained are to be regarded as the minimum values, and the molecular weight must be multiplied by

a factor n , where n may be any integer.

Sec. VI. The Relation between Fibroin and Sericin.

Shelton and Johnson⁽⁶⁴⁾ showed that fibroin is probably a mixture of proteins loosely combined with one another. From the microscopical and chemical investigations we can presume that most of amino-acid components of silk fibroin consist of the main-axis components like glycocoll,

(63) Block and Vickery, *J. Biol. Chem.*, **93** (1931), 105, 113.

(64) Shelton and Johnson, *J. Ind. Eng.*, **22** (1930), 337.

alanine, etc. and a part of it consists of the side-chain components which are similar to those of sericin. The following orders hold good: fibroin $>$ sericin A $>$ sericin B, in main-axis components, fibroin $<$ sericin B $<$ sericin A, in side-chain components. The first order may be parallel with the easiness of precipitation with $(\text{NH}_4)_2\text{SO}_4$, and the second with their solubilities.

The solubility of sericin may depend for the most part on its basic components. And on boiling the sericin solution, the basic side-chain components may gradually separate off and the degree of hydration may be diminished. Therefore, the viscosity of the sericin solution may gradually diminish on boiling, and gelatinization may become imperfect. Then, the solubility of sericin in water may depend on the quantity of sericin, especially of sericin A, existing on the cocoon fibre and also on the quantity of the basic components.

Though the solubility of sericin increases on boiling under pressure, sericin B and a part of amorphous components of silk fibroin which are similar to those of sericin B may be dispersed into the solution. This may lead to decrease in the strength, elongation, and luster of silk fiber. For the same reason the ferment which decomposes the sericin B especially may also be able to attack on the amorphous components of fibroin, and the similar bad effects may be caused in the silk fiber.

Tyrosine contents of sericins and fibroin. Sericin was hydrolysed by six hours boiling with 25 per cent. sulphuric acid six times as much as the quantity of the sericin, the solution, after filtration, was diluted with twice its volume of water and neutralized with a strong solution of baryta, the excess of which was then quantitatively removed by dilute sulphuric acid. The solution, together with the water used for thoroughly washing the precipitate of barium sulphate, was then evaporated, until tyrosine crystallized out. It was collected; the filtrate was concentrated, and further crops of crystals were obtained until the mother liquor gave no longer

Millon's reaction for tyrosine. It was purified by recrystallization from water, decolorization of the solution being effected by charcoal.

The tyrosine content of fibroin is on an average about 10 per cent., and it is a few times as great as that of sericin.

Table 110.

	Tyrosine	Gly./Tyr.
Sericin A	2.62%	2.38
Sericin B	5.53	0.84
Sericin (Abderhalden)	3.50	—
Fibroin (,)	11.00	3.59

Sericin B contains much more tyrosine component than sericin A. The value of glycine : tyrosine is the greatest in fibroin, next in sericin A, and the least in sericin B. The above results lead to the conclusion that sericin is characteristically rich in side-chain components which have the great affinity with water, that fibroin is richer, on the contrary, in the main-axis components, and that in the distribution of nitrogen in the side-chain components sericin B is similar to the amorphous components of fibroin.

As is well known the high temperature and high relative humidity influence greatly the spinning velocity of liquid silk by silk worms. Y. Tanzawa⁽⁶⁵⁾ showed that the spinning velocity was proportional to the temperature under the same conditions. The greater the spinning velocity becomes, the more sericin B which is considered to exist closely near the fibroin layer is spun out. Then the quantity of sericin B contained in the outer layer of cocoons increases with rising temperature, and this causes the retardation of the gelatinization of silk owing to the nature of sericin B, especially at high relative humidity. These unfavourable conditions may cause firm adherence of fibers and make them thinner.

PART III. CONCLUSION.

Sec. I. Varieties of Sericin.

The varieties of sericin which have been reported are summarized in Table 111.

Table 111.

Author	Varieties of sericin
K. Kodama	Sericin, Sericin pepton
K. Kondo	Sericin I, Sericin II.
Shelton and Johnson	Sericin A, Sericin B.
H. Kaneko	Sericin A, Sericin B.
T. Watanabe	Alcohol soluble and insoluble sericins.

K. Kondo prepared sericin for examination by soaking silk in water and treating it under 2.5-3 atmospheric pressures of steam for three hours. After three such treatments the water-soluble fraction was concentrated and the sericin was precipitated by adding two volumes of 80 per cent.

(65) Y. Tanzawa, *Sangyo Shimpô*, 1930, No. 448.

alcohol. This sericin was washed thoroughly with absolute alcohol and ether, and designated as sericin I. Sericin II was obtained by further concentrating the alcoholic filtrate and treating the concentrate with 80 per cent. alcohol. The resulting precipitate, washed with absolute alcohol and ether, gave a yellow powder.

Shelton and Johnson extracted sericin from silk with a small amount of water under a pressure of 50 cm. of mercury. They found that the whole protein was precipitated by means of alcohol and that after precipitation only a portion would again dissolve in cold water. They also found, as in the case of fibroin, that varying concentrations of $(\text{NH}_4)_2\text{SO}_4$ gave two kinds of precipitates, the first being a gelatinous substance insoluble in cold water.

T. Watanabe obtained two sericins from the sericin solution with alcohol. One was insoluble in 50 per cent. alcohol, and the other soluble in it. The results lead to the conclusion that sericin is not a simple compound, but it is a mixture of at least two different substances.

When I investigated the physico-chemical properties of the sericin solutions obtained from the cocoons having various "kaijo", I noticed many differences in their behaviours, though these differences may be partly due to the impurities contained in the cocoon layers. Then I obtained two different sericins from the sericin solution by the fractional precipitation with $(\text{NH}_4)_2\text{SO}_4$ as done by Shelton and Johnson. But I further found that the separation into these two components can be effected also by other electrolytes, by freezing, and by the electric current. The one which was easily salted out from solution by electrolytes was named "sericin A" and the other "sericin B." These two sericins were similar in the distribution of various forms of nitrogen, but very different in their physical properties.

Sec. II. The Distribution of Two Sericins on the Cocoon Fibers.

The distribution of sericin A and sericin B on the cocoon fibers has an intimate relation with the "kaijo" of cocoons, because they have different physico-chemical properties. The relation between the proportion of two sericins and "kaijo" are given in Table 112.

The better "kaijo" a cocoon has, the more sericin A is contained. H. H. Mosher⁽⁶⁶⁾ estimated two sericins in several raw silks by boiling cocoons in water at 115°C. under pressure.

In the same cocoon the outer layer is rich in sericin A and the inner layer in sericin B. So when we intend to reel cocoons at low temperature,

(66) H. H. Mosher, *American Dyestuff Reporter*, No. 11, 1932.

we must bear it in mind that the inner layer containing more sericin B should be thoroughly cooked.

Table 112.

" Kaijo "	Sericin A	Sericin B
Good	61.23%	38.76%
Middle	55.22	44.78
Bad	43.32	56.68

These two sericins seem to exist already in the liquid silk of the silkworm, and these may probably be secreted from different parts of the silk gland. Therefore, the " kaijo " of cocoons may primarily depend on the varieties of the cocoons and secondarily on the external conditions during the spinning of liquid silk and physical treatments.

The temperature influences the speed of spinning of liquid silk and may cause a change in the proportion of two sericins. The high relative humidity during the spinning retards the evaporation of water and consequently the gelatinization. Especially, heat may cause the transformation of sericin A into sericin B, so we must take care when we dry cocoons.

In gelatinization the inner and middle layers of cocoons are placed in worse conditions than the outer and further they may easily absorb the fatty matter from the pupa. These may lead to worse " kaijo."

Sec. III. The Micellar Structure of Sericins and Their Physico-Chemical Properties.

It has been considered that sericin is an amorphous substance. Although sericin and fibroin have remarkably different appearance, a micellar structure can be presumed for sericin, especially sericin A, as for the fibroin. The difference in the characteristic behaviours of these two proteins may be due to the difference in the proportion of the main-axis and side-chain components. Naturally fibroin is richer in the former component and sericin in the latter which has great affinity with water. As already described sericin A is coagulated in a fibrous form by many electrolytes, by freezing, and by applying the electric field in the sericin gel. The coagulate is considered to have a micellar structure.

The experiment concerning the distribution of various forms of nitrogen in sericin A and sericin B has shown that in the former more basic amino-acids are contained than in the latter. For this reason sericin A may be stronger hydrated in aqueous solution and in fact it shows higher viscosity, stronger swelling capacity, easier gelatinization, and heavier apparent specific gravity than sericin B.

Sericin A is apt to denature on drying, to turn slightly gray, and to shrink easily to a hard mass. Hence the solubility of sericin A in water is greatly reduced by drying though it seems that it ought to be more soluble than sericin B.

By the X-ray analysis of sericin powder it is shown that sericin has no micellar structure. But, it seems to me that this is the result of the shrinking property of sericin A as in the case of not stretched caouchouc. Recently K. Obara also has advanced the same opinion for the existence of a micellar structure in sericin on the ground of his microscopical

Table 113.

	With increasing concentration, near 0.3%
Relative viscosity	rapidly increases
Surface tension	rapidly decreases
Diffusion coefficient	„ „
Specific rotation	„ „
Electric spec. conductivity	rapidly increases
Flocculation value	„ „
Gelatinization capacity	„ „
Depression of freezing point	„ „

investigation. Electrically charged sericin which tends to form molecular aggregates in solution, exists in solution as comparatively large particles associated with very large quantities of water. This aggregation of the sericin micellæ in aqueous solution varies with concentration and also with time. The physico-chemical properties of the sericin solution change, therefore, rapidly

near the concentration of 0.3 per cent. as shown in Table 113. Effects of time of standing at the same concentration are given in Table 114.

Table 114.

	Maximum	Conc. (%)
Relative viscosity	about 90 min. later	0.32
Lowering of surface tension	„ 35 „ „	0.40
Electric spec. conductivity	„ 30 „ „	0.53
Gelatinization capacity	„ 120 „ „	1.18
Protection against the decomposition of H_2O_2 by Pt sol	„ 90 „ „	0.4-0.3

The aggregation of sericin micellæ depends also greatly on the temperature at the same concentration. From other experiments I can presume that the temperature of transformation of sol into gel corresponds to about 50°C.

Sec. IV. The Isoelectric Point of Sericin.

At the isoelectric point the dissolved protein is all electrically neutral. Such a solution is characterized by the tendency to aggregate and to take a high degree of turbidity and by the maximum ease in precipitation with alcohol or other lyophilic reagents. It has a greater surface activity. Dissolved protein always lowers the surface tension of water, but the effect is the greatest at the isoelectric point and is, therefore, due more to the electrically neutral protein than to the electrically charged. Hardy showed that the position of the maximum precipitation is influenced by the salt content. The isoelectric points obtained by various experiments are shown in Table 115 and 116.

Table 115. The isoelectric point of the natural sericin (mixed sericin).

	Good	Middle	Bad	Conc. (%)
Minimum relative viscosity	pH 3.95	4.12	4.18	0.2
Minimum surface tension of water	4.25	4.30	4.40	0.08
Minim. spec. rotation	4.24	4.30	—	0.2
Minim. emulsifying power	4.0	4.5	4.8	0.13
Maxim. precipitability with				
Methyl alcohol	4.0	—	—	0.2
Ethyl alcohol	3.8	—	—	„
Acids	3.9	—	—	„
FeCl ₃ , AlCl ₃ , etc.	4.2	—	—	„
Nitrates	4.6	—	—	„
Acetone	4.0	—	—	0.12
Minim. cataphoretic velocity	4.35	4.45	4.45	

Table 116. The isoelectric point of sericin A and sericin B.

	Sericin A	Sericin B
Minim. swelling	pH 3.80	4.50
Maxim. degree of turbidity	4.05	4.20
Minim. cataphoretic velocity	4.10	4.25
Minim. solubility	4.50	4.70

The isoelectric point of the natural sericin in which sericin A and B are mixed depends on the concentration and also on the "kaijo" of cocoons. In low concentrations the isoelectric point corresponds to about pH 4.0 in the sericin solution obtained from cocoons of good "kaijo", and it is shifted to the alkaline side in the solution obtained from cocoons of bad "kaijo".

The isoelectric points of sericin A and sericin B are respectively about pH 3.8 and pH 4.50. So we can understand that the isoelectric point of the sericin solution varies with the "kaijo" of cocoons, and that the sericin solution shows usually the isoelectric range in which sericin is capable of being precipitated by the addition of electrolytes or alcohol. If these two sericins are contained in equal amounts in the sericin solution, its isoelectric point may be probably pH 4.15.

Sec. V. The Molecular Weight of Sericin.

The probable molecular weight of sericin micellæ calculated from various data are given in Table 117. From these results the molecular weight of the sericin micellæ is considered to have an order of ten thousand.

Table 117. Molecular weight of sericin = $403 \times n$.

Calculated from	Mol. wt.	n
Viscosity	4026 (0.35%)	10
Diffusion coefficient	29441 (0.38%)	73
Depression of f. p.	8936 (0.34%)	22
Chemical analysis	19129 (sericin A)	47

Sec. VI. The Fibroin and Sericin, Two Proteins of Silk.

As shown by R. Inoue, fibroin and sericin are similar in the distribution of various forms of amino-acids, but very different in the proportion of the main-axis and the side-chain components. So the difference between fibroin and sericin exists in the proportion of components, their arrangement, and the manner in which they are linked.

The amorphous side-chain components of fibroin are especially similar to those of sericin B. The complete separation of sericin B from fibroin without doing damage to fibroin components may be theoretically difficult.

The formation of a film which protects the fibroin fiber must be necessary for the existence of sericin A which has probably a micellar structure.

In conclusion the author wishes to express his cordial thanks to Prof. Y. Shibata for his kind guidance and encouragement.

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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH.

IX. THE PROMOTION AND POISONING OF THE CATALYTIC ACTION.*

By Koshiro ISHIMURA.

Received July 26th, 1934. Published December 28th, 1934.

The behaviours of the chief constituents of Japanese acid earth in its catalytic action on naphthalene have been elucidated,⁽¹⁾ but the rôle played by water contained in the earth has been left untouched. It has now been found that water exerts a distinct promoting action in that catalysis. Several neutral substances containing oxygen in their molecules such as methyl and ethyl alcohols, acetone, and ether have also proved to be promoters similar to water, and those which contain nitrogen such as ammonia, methylamine, acetonitrile, and amyl nitrite behave as strong poisons, while acidic substances such as hydrogen chloride and acetic acid are quite weak poisons. Chloroform, carbon tetrachloride, chlorobenzene and many hydrocarbons have been found indifferent to the catalytic action.

The acid earth used almost exclusively in the present experiment is that which has been designated earth F in the previous papers, and its catalytic activity on naphthalene measured by the yield of the resinous matter under the "standard condition" is, as stated in the previous paper,⁽²⁾ 2.23. This value was taken as the standard for the comparison of the activity throughout the present experiment, unless specially mentioned.

The Action of Water. With the rise in the drying temperature of the acid earth its catalytic activity decreases rapidly, the liberation of water from the earth being observed simultaneously as shown in Fig. 1 and Table 1.⁽³⁾

The experiments were carried out under the "standard condition" in the determinations of the activities except that the samples were dried at respective temperatures for one hour. The amounts of water set free were estimated after the constant weights were obtained at respective temperatures.

* An epitomized translation of the original published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue and Ishimura, This Bulletin, **9** (1934), 431.

(2) Loc. cit.

(3) 97 Per cent. or more of the ignition loss is due to the liberation of water. Kobayashi, Yamamoto, and Bito, *J. Soc. Chem. Ind. Japan*, **32** (1929), 998.

Table 1.

Temp. of drying	To 50°	50-120°	120-200°	200-250°	250-300°	300-500°	Above 500°
Water set free (%)	3.33	3.73	0.76	0.62	0.27	1.03	3.97

The decrease in the catalytic activity of the earth shown in Fig. 1 may not be ascribed only to the effect of the heat treatment, since water may

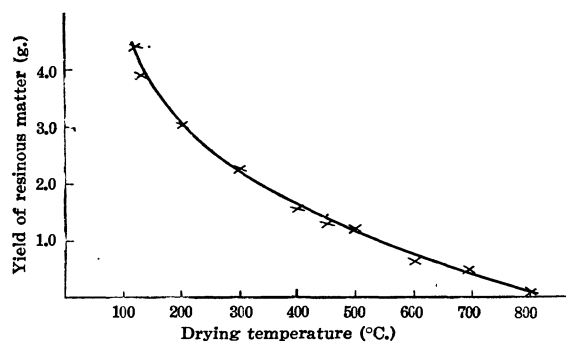


Fig. 1.

play some rôle in the catalysis. In order to ascertain whether water influences the catalysis or not, it is necessary to procure the specimens of the earth containing the different amount of water with the same heat treatment. The earth dried at 300° adsorbs water vapour rapidly when brought into contact with the saturated vapour at room temperature

and when the moist earth thus obtained is dried again at 120° it liberates almost all the water adsorbed, but a small fraction of it is always held by the earth even after the drying is continued for about 10 hours until the weight of the earth becomes constant. The water retained at the end of this treatment will be hereafter called, for convenience' sake, "retained water".

The amount of the retained water is a function of the total amount adsorbed as shown in Fig. 2. Thus several samples of the earth with different water content after the same heat treatment are obtainable, and it will be safely stated that if their catalytic activities under the same condition differ from one another it may be entirely ascribed to the difference of the amount of water contained in them.

The relation between the amount of the retained water and the cataly-

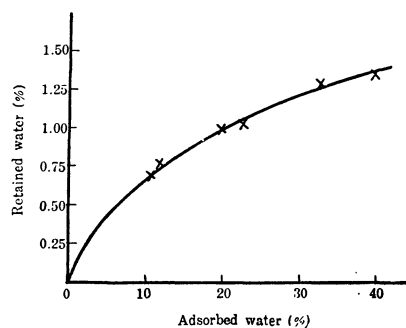


Fig. 2.

tic activity is shown in Table 2, which indicates that the larger the former is the greater the latter, in other words, the retained water exerts a decided promoting action in the catalysis.

Table 2.

Time of adsorption (days)	0	10 (hrs.)	1	7	13	21	33
Water adsorbed (%)	0	5.16	9.42	22.8	26.3	32.9	38.9
Water retained (%)	0	0.66	1.06	1.35	1.47	1.69	1.87
Yield of resinous matter (g.)	2.23	2.49	2.75	3.08	3.08	3.42	3.59
Increase in resinous matter (g.)	—	0.26	0.52	0.85	0.85	1.19	1.36

Though about 10 hours are required to get the constant weight when the moist earth is dried at any temperature, about 98 per cent. or more of the total water to be liberated is set free within 2 hours. The amount of the retained water after 5 hours' drying are plotted in Fig. 2 and those after 2 hours' drying are tabulated in Table 2, and in all the experiments described below the duration of drying was fixed at 2 hours.

The catalytic activities of the earth treated at 500° and 800° are also promoted by the retained water as shown in Table 3.

Table 3.

Temperature of pre-treatment	500°				800°	
Time of adsorption (days)	0	2	2 ⁽⁴⁾	16	0	18
Water adsorbed (%)	0	9.01	15.1	22.2	0	9.0
Water retained (%)	0	0.26	0.39	0.55	0	0.2
Yield of resinous matter (g.)	1.20	1.66	1.95	2.06	0.11	0.17
Increase in resinous matter (g.)	—	0.46	0.75	0.86	—	0.06

(4) Owing to the differences of temperature and vapour pressure, the different values of adsorbed water are obtained after equal time of adsorption.

If a represents the yield of the resinous matter produced by the earth and b the increase in the yield caused by the retained water, then a quantity

$(b/a) \times 100$ may be designated "degree of promotion". The degrees of promotion calculated from the data given in Table 2 and 3 are plotted against the amounts of the retained water expressed in millimols as shown in Fig. 3.

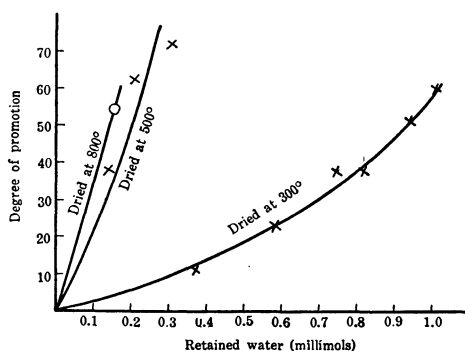


Fig. 3.

The water simply adsorbed by the dry earth as well as that added in the reaction tube in liquid state also promotes the reaction, but their promotive powers fall far behind that of the retained water as will be seen in Table 4.

Table 4.

Kind of water	Retained	Adsorbed	Added	Retained	Added
Amount of water (%)	1.70	1.99	1.93	1.87	5.14
Yield of resinous matter (g.)	3.38	2.31	2.31	3.59	2.87
Increase in resinous matter (g.)	1.15	0.08	0.03	1.36	0.45

Now, when the desorption of water from the moist earth takes place, the molecules of water stored in large capillaries in liquid state or those localized on the upper layers of the adsorbed film would be liberated first, and those held directly on the bare surface would remain to the very last, representing the retained water above designated. The data given in Table 4 seem to show that it is these water molecules adsorbed directly—therefore the most firmly held—on the surface that promote the catalysis but not those more loosely adsorbed or those simply present in the reaction system.

If, in the course of the adsorption, the monomolecular film of water is formed on the whole surface before there occurs the formation of any polymolecular film, the amount of the retained water would represent the total amount of the water adsorbed in the early stage of the adsorption and the former would become independent of the latter if once the whole surface is covered. As a matter of fact, however, this is not the case. As will

be suggested in next communication, the amount of water needed to cover the whole surface of the dry earth represents about 2.5 per cent. of the weight of the earth on the assumption of a packed monomolecular layer. Fig. 2 and Table 2 show that the proportionality between the amount of retained water and the total amount adsorbed extends far above this limiting value. It would appear therefore that the formation of the polymolecular layers as well as capillary condensation commences long before the whole surface is covered with a monomolecular layer. Hoover and Rideal⁽⁵⁾ came to the same conclusion from a different view point in the case of the adsorption of ethyl alcohol on thoria.

The Actions of Oxygen-containing Neutral Substances other than Water. Methyl and ethyl alcohols, acetone, and ether were examined and all of them were found to promote the reaction to a marked degree. All materials were cautiously purified by appropriate methods. The adsorption of vapours was carried out in a desiccator at saturated vapour pressures and the retained amounts were determined by the same method as the above-mentioned. As in the case of water, the amount of each retained substance was found to be a function of the total amount adsorbed. The plots of degrees of promotion against the retained amounts expressed in millimols of the respective substances are shown in Fig. 4.

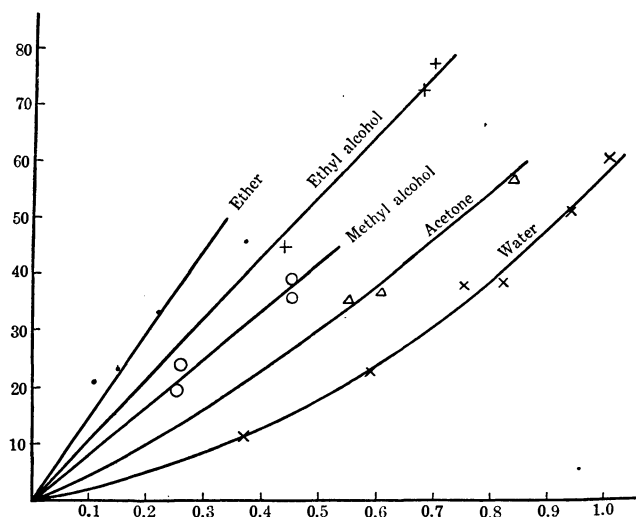


Fig. 4.

(5) *J. Am. Chem. Soc.*, **49** (1927), 122.

The order of magnitudes of the degrees of promotion corresponding to the same millimols of the retained substances can be easily given from Fig. 4 as follows :—

Ether > ethyl alcohol > methyl alcohol > acetone > water.

Gurwich⁽⁶⁾ has studied the heats of adsorption of various organic liquids when brought into contact with Fuller's earth⁽⁷⁾ as well as the dispersive powers which were measured by the percentage of Fuller's earth remaining in suspension in those liquids after shaken up with them. The results of his determinations⁽⁸⁾ are given in the second and third columns of Table 5.

Table 5.

Substance	Heat of adsorption	Dispersive power (%)	Dielectric const. (18°)	Surface tension (20°) ⁽⁹⁾	Solubility of naphthalene (0°) ⁽¹⁰⁾
Ether	10.7	0.90	4.36	16.49	large
Ethyl alcohol	17.2	—	20.8	22.03	0.0209
Methyl alcohol	21.8	1.60	31.5	23.02	0.0087
Acetone	27.3	1.72	21.5 (20°)	23.35 (16.8°)	—
Water	30.2	2.85	81.1	70.60	0.0000

The order of the magnitudes of both the heats of adsorption and dispersive powers determined by Gurwich is exactly reverse to the order of the degrees of promotion observed by the present author. The regularity of this relation is very striking. It is also noticed that the solubility of naphthalene, the dielectric constant, and the surface tension of the liquids go either parallel or reverse to the degree of promotion as shown in Table 5.

(6) *J. Russ. Phys. Chem. Soc.*, **47** (1915), 805.

(7) Japanese acid earth is in many respects similar to Fuller's earth, and it is generally accepted that the former is a species of the latter.

(8) Cited from Langmuir's paper. *J. Am. Chem. Soc.*, **39** (1917), 1898.

(9) This column represents the surface tensions expressed in dynes per cm. in the atmospheres of the saturated vapours of the respective substances.

(10) The solubility of naphthalene is expressed in mols per mol of the respective solvent. The solubility in acetone is not found in literature, so far as the author knows.

As will be fully discussed in next communication, the catalytic action of Japanese acid earth on naphthalene may be considered to be brought about by the three component catalyst consisting of Al_2O_3 , SiO_2 , and water, and when molecules of naphthalene are adsorbed on the catalytically active centres formed by these three components they are activated so as to produce β, β' -dinaphthyl. When the earth is heated to 300° the liberation of water from some of these active centres takes place rendering them incapable of participating in the catalysis. They will, however, recover their ability if water molecules are again put in their original positions. This recovery of catalytic activity is accomplished by the retained water when the earth is brought into contact with water vapour, giving rise to the observed promotion of the activity. Moreover, the molecules of water to form the active centres are replaceable by those of neutral substances such as alcohols, acetone, and ether, and the similar promoting action is effected by them.

The degree of promotion depends therefore upon both the number of the active centres thus recovered and the number of molecules of naphthalene to be activated on each of these new centres, in other words, upon the number and the intensity or the mean life of new active centres.

Table 5 shows that, the greater is the degree of promotion the smaller the heat of adsorption and the dispersive power and the larger the solubility of naphthalene. The heats of adsorption and the dispersive powers would be considered as measures of the molecular affinities between these various liquids and the acid earth, while the solubilities of naphthalene as measures of the molecular affinities between these liquids and naphthalene. The author is inclined to believe that the former is connected with the number of the active centres to be recovered and the latter with the intensity or the mean life of these centres to activate the molecules of naphthalene adsorbed on them, that is, the larger the molecular affinity between the vapour and the acid earth the more difficult becomes the formation of the active centres, and the larger the molecular affinity between the vapour and naphthalene the stronger is the intensity or the longer is the mean life of the active centres. Dielectric constant and surface tension are in close connection with the molecular structure and the orientation of molecules on the surface of liquids respectively, and it may be anticipated that these quantities would bear some relationship with the catalytic activity.

It is tempting to go on studying how Al_2O_3 , SiO_2 , and oxygen-containing neutral substances must be configured in order to form the active centres and how molecules of naphthalene must be oriented on them in order to be activated, and further study on these lines is expected to be carried out in near future.

The Action of Hydrogen Chloride, Acetic Acid, and Ethyl Acetate. The acidic substances such as hydrogen chloride and acetic acid (and most probably hydrogen sulphide, too) are quite weak poisons to the catalytic action. Their total amounts adsorbed are fairly small compared with the neutral substances. Table 6 shows the results of experiments on these substances as well as ethyl acetate.

Table 6.

Substance	Hydrogen chloride		Acetic acid	Ethyl acetate
Amount adsorbed (%)	2.23	—	5.96	20.03
Amount retained (%)	0.33	1.21 (added)	5.58	4.20
Amount retained (millimol)	0.09	0.33	0.93	0.48
Yield of resinous matter (g.)	2.25	2.01	2.01	2.44
Decrease in yield (g.)	0	0.22	0.22	0.21 (increase)
Decrease in yield (%)	0	10	10	10 (increase)

Ethyl acetate is a neutral substance and moreover values of both the heat of adsorption and dispersive power determined by Gurwich lie between those of methyl alcohol and ether; therefore it seems very reasonable that it would make a promotor as strong as the alcohol at least. The fact is, however, that it proved to be a very weak promotor as will be seen from Table 6. This may be explained by the experiment by Dr. Inoue⁽¹¹⁾ that ethyl acetate is decomposed by the catalytic action of Japanese acid earth giving acetic acid, the poison to the reaction.

The Actions of Nitrogen-containing Substances. Ammonia and methylamine are the most strong poisons, while acetonitrile and amyl nitrite are milder in their poisoning actions as shown in Table 7.

(11) *J. Soc. Chem. Ind. Japan*, **28** (1925), 598.

Table 7.

Substance	Ammonia	Methylamnie	Acetonitrile	Amyl nitrite
Amount adsorbed (%)	5.49	5.66	27.06	61.05
Amount retained (%)	0.84	4.45	3.08	16.02
Amount retained (millimol)	0.49	1.43	0.75	1.36
Yield of resinous matter (g.)	0	0	0.28	0.23
Decrease in yield (g.)	2.23	2.23	1.95	2.00
Decrease in yield (%)	100	100	88	90

The Actions of Hydrocarbons, Chlorine-containing Neutral Substances, and Thiophene. It should be noted that the retained amounts of these substances are in general very small unless the adsorbed substance is decomposed by the catalytic action of the earth at room temperature as in the case of alicyclic unsaturated hydrocarbons. Benzene, toluene, cyclohexane, cyclohexene, and methylcyclohexenes were examined and all of them were found to be indifferent to the reaction. It does not matter whether these substances were retained, adsorbed or added or entirely absent. The yield of the resinous matter was always equal within the experimental error. Chlorobenzene behaves similarly. Chloroform and carbon tetrachloride are also indifferent as long as their amounts are small, but if they are added in relatively large quantities the yield of the resinous matter is decreased to some extent, the evolution of hydrogen chloride being observed simultaneously. It appears therefore that they are non-poisonous in themselves, and their apparent poisoning action is to be ascribed to hydrogen chloride produced by the catalytic action of the earth.

The experiments hitherto carried out with thiophene are not sufficient to draw any decided conclusion thereby. It may be only mentioned here that when thiophene is added in fairly large quantity the slight poisoning effect is observed, accompanied by the evolution of hydrogen sulphide.

Summary.

(1) The catalytic action of Japanese acid earth on naphthalene is greatly promoted when it contains the "retained water", designated temporarily by the present author.

(2) The molecules of the "retained water" may be replaced by those of several other neutral substances containing oxygen in their molecules, the catalytic activity of the earth being thereby raised to a greater or smaller extent according to the nature of the substance.

(3) The term "degree of promotion" has been introduced, and the relation between the degree of promotion and molecular affinity has been discussed.

(4) The nitrogen-containing substances such as ammonia, methylamine, acetonitrile, and amyl nitrite have been found to be strong poisons to the catalysis, while the acidic substances such as hydrogen chloride and acetic acid have proved to be quite weak poisons.

(5) Chloroform, carbon tetrachloride, chlorobenzene, and many hydrocarbons have been found indifferent to the catalytic action.

The author wishes to express his cordial thanks to Dr. Inoue for his interest and encouragement taken in this study.

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THE BENZYL ETHERS OF POLYSACCHARIDES. I.
THE BENZYL ETHERS OF STARCHES OF VARIOUS ORIGINS.

By Tei-ichi ASAHINA and Gengo NARA.

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The preparation of benzyl ethers of mono- and poly-saccharides was first reported by Gomberg and Buchler.⁽¹⁾ Of those, cellulose benzyl ethers have been continually studied and proved to give products of good quality. At present they are manufactured to reply the demand as lacquer constituents. The benzyl ethers of other polysaccharides, however, have scantily been investigated.⁽²⁾

(1) M. Gomberg and C. C. Buchler, *J. Am. Chem. Soc.*, **43** (1921), 1904.

(2) Brit. P., 149320 (1921); Lilienfeld, D.R.P., 360415 (1922); F.P., 534778 (1921); I.G. Farbenindustrie, Austrian P., 12780 (1932).

Gomberg and Buchler reported that, under their experimental conditions, the benzyl ether obtained from potato starch was not identical with that from corn starch in respect of the composition. From potato starch they obtained monobenzyl ether of the composition corresponding to $C_{12}H_{19}O_{10} \cdot C_7H_7$, while from corn starch, dibenzyl ether of the composition corresponding to $C_{12}H_{18}O_{10} \cdot 2C_7H_7$. They do not seem to have made much further studies on these two different ethers: their melting points and solubilities in some organic solvents did not differ much from each other. There is, however, no explanation by those authors on the difference in behaviours of the different kinds of starches. It is interesting that the starches from different origins gave products of different degrees of benzylation under the same conditions. From this point of view we have undertaken the benzylation of starches from various plants, as they are easily accessible in our country.

For the present, the potato starch, corn starch, wheat starch, "Kuzu-ko" (starch powder prepared from the root of *Pueraria triloba*, MAKINO) and "Warabi-ko" (starch prepared from the root of *Pteridium aquilinum*, KUHN, var. *japonicum*, NAKAI) have been brought under investigation.

Alien from the results reported by Gomberg and Buchler, these starches gave exclusively the dibenzyl ethers of the composition corresponding to $C_{12}H_{18}O_{10} \cdot 2C_7H_7$ under our experimental conditions which did not differ much from those mentioned by them. At first our results of elementary analyses of the products corresponded neither to mono- nor to di-benzyl ether of starch, but on strictly desiccating them, the figures obtained were quite identical with those calculated for dibenzyl ether, well within the limit of experimental errors. The melting points of the products were either discordant from those observed by Gomberg and Buchler. Though the melting points of such amorphous substances cannot be generally expected to be very sharp, the discordance was very much remarkable. Of all the products the melting points were found to lie between 165° and 175° . Furthermore we made polarimetrical measurements of the benzyl ethers from various starches, which showed nearly the same rotatory power.

From our experiments, we cannot definitely gainsay the results obtained by Gomberg and Buchler, but there can be some doubtful points there.

Whether our products which we consider to be dibenzyl ethers from the figures of elementary analyses only, are really so, or mixtures of benzyl ethers of different degrees of benzylation, cannot be determined from the results so far obtained. The matter needs further study, and shall be treated in following reports.

Experimental.

(1) **Preparation of Benzyl Starches.** The starch was dried in an air-oven at 80–90° for some hours. To 1 mol (8 g.) of the dried starch, 4.5 mols (9 g.) of 9% caustic soda and 3.5 mols (22 g.) of benzyl chloride were added. They were well blended in a wide-necked conical flask by shaking vigorously; thus a thick, translucent, homogeneously dispersed liquid was obtained which was heated under occasional shaking in a water bath kept at 80–85° about four hours. In the course of one hour and a half a gummy mass separated and after that no remarkable change was observed. The mode of reaction was nearly the same for all the species of starch used.

(2) **Purification of the Products.** The solution was decanted from the gummy mass and the latter was subjected to steam distillation to remove occluded benzyl chloride and some impurities produced during the reaction. The mass did not come to pieces and the trace of the impurities could not be removed in this way. The steam distillation was stopped; the mass in the flask was drained and pulverised in the mortar with the addition of a small quantity of ether to dissolve the impurities. After repeated washing with fresh ether, the powder was dried in the air-oven at 80–90°. The yield is shown in Table 1, that calculated for mono- and di-benzyl ethers being 10.2 g. and 12.4 g. respectively.

Table 1.

Origin of starch	Potato	Corn	Sweet potato	Wheat	“Kuzu”	“Warabi”
Yield of benzyl ether	11.7 g.	11.4 g.	11.2 g.	11.0 g.	11.3 g.	11.2 g.

The crude products were all more or less discoloured to slightly yellow; the discoloration of that from “Warabi” starch was the most remarkable. The product was dissolved in a small quantity of glacial acetic acid and filtered from minute fragments of insoluble matters through a hot funnel. To the filtrate, pure ether sufficient to precipitate the product was added. The supernatant ethereal solution was decanted and the separated white powder was repeatedly washed with fresh ether to remove the trace of acetic acid. The repetition of the procedure seems to give products of no further purity when we judge from the data of elementary analyses and the inspection of the melting points. The product from “Warabi” starch was three times precipitated in this way.

(3) **Elementary Analyses.** The elementary analysis is the only simplest way to determine the degree of benzylation.⁽³⁾ The product was dried in the air-oven at 80–90° until the weight was constant and it was kept in the desiccator. Before analysis, the sample was dried in Abderhalden's desiccating apparatus in vacuo at 110°; the figures (Table 2) given in the columns designated by I were calculated, with the correction of moisture content, from the values obtained with the samples which were not dried in Abderhalden's apparatus. The mean value of the carbon content lies between 60.43 and 60.78% and that of hydrogen between 6.35 and 6.53% and they are well coincident with those calculated for $C_{12}H_{18}O_{10} \cdot 2C_7H_7$ (C, 61.92; H, 6.35%), and not for $C_{12}H_{18}O_{10} \cdot C_7H_7$ (C, 55.07; H, 6.28).

Table 2. Analyses of Benzyl Ethers from

Potato Starch

	H (%)	C (%)	Ash (%)
I	6.44	60.80	—
	6.59	60.79	—
II	6.37	61.48	0.3
	6.51	60.22	—
	6.66	61.01	0.4
	6.60	60.65	—
	6.53	60.52	0.3
Mean	6.53	60.78	0.3

Corn Starch

	H (%)	C (%)	Ash (%)
I	6.49	61.05	—
	6.55	60.88	—
	6.32	60.70	—
II	6.54	61.18	—
	6.26	60.69	—
	6.34	60.15	0.4
Mean	6.42	60.78	0.4

Sweet Potato Starch

	H (%)	C (%)	Ash (%)
I	6.26	59.79	—
	6.45	60.74	—
	6.29	60.64	—
	6.25	60.31	—
II	6.44	60.64	0.4
	6.40	60.37	0.4
	6.37	60.54	—
Mean	6.35	60.43	0.4

Wheat Starch

	H (%)	C (%)	Ash (%)
I	6.57	61.41	—
	6.74	60.99	—
	6.45	60.52	—
	6.41	60.03	—
	6.31	59.99	—
II	6.53	61.28	—
	6.46	60.45	—
	6.46	60.14	0.3
Mean	6.49	60.60	0.3

(3) The method proposed by Meunier and Gonfard seems rather tedious. *Compt. rend.*, **134** (1932), 1839.

Table 2. (*Concluded*)

"Kuzu" Starch				"Warabi" Starch			
	H (%)	C (%)	Ash (%)		H (%)	C (%)	Ash (%)
II	6.37	60.93	—	II	6.46	60.69	—
	6.69	60.76	0.3		6.69	60.39	—
	6.31	60.41	0.4		6.14	60.57	0.5
Mean	6.46	60.70	0.4	Mean	6.43	60.55	0.5

(4) **Melting Points and Specific Rotations.** These are shown in Table 3. In the measurement of optical rotations, ethylene chlorohydrin of b.p. 127.5–128.5° was used as the solvent, the concentration being about 3 per cent. and the temperature about 30° (Table 3).

Table 3.

Origin of starch	Melting point (°C.)	Rotation		
		Conc. (g./dl.)	Temp. (°C.)	[α] _D
Potato	170–172	2.986	30.6	+118.3
Corn	170–172	3.025	30.7	+120.1
Sweet potato	169–172	3.013	30.8	+117.1
Wheat	169–171	3.015	31.1	+120.8
"Kuzu"	165–169	3.003	31.2	+118.5
"Warabi"	170–172	3.000	31.1	+118.1

As the light-source for the polarimetric measurement, we used a sodium-flame produced by a glass-work burner: a pinch of asbestos wetted with a strong solution of sodium carbonate or caustic soda and dried in the flame of a Bunsen burner, is fastened with copper wire and put into the flame near the jet of the glass blowing burner. Instead of air blast, a moderate stream of oxygen is supplied from the bomb. The brightness of the light source is comparable with that of a small electric sodium lamp.

Quite recently A. I. Schattenstein⁽⁴⁾ reported an analogous idea on the use of oxygen-coal-gas flame as a monochromatic light source of D-line. Sodium chloride and bromide which he used cannot be recommended, for, although the intensity of the flame is great, much smoky sublimate is produced and this makes the air of the laboratory very dirty.

(4) A. I. Schattenstein, *Z. anal. Chem.*, **98** (1934), 235.

STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS.
PART VIII. ELECTROLYTIC OXIDATION OF
HISTAMINE AND HISTIDINE.

By Yoshitaro TAKAYAMA and Haruomi ÔEDA.

Received September 7th, 1934. Published December 28th, 1934.

In a previous communication,⁽¹⁾ it was stated that imidazolyl-propionic acid was readily oxidized at the anode and the rupture of imidazol nucleus resulted. In the present paper studies on histamine and histidine are reported and the mechanism of oxidation of these three kindred compounds are discussed. They have the same heterocyclic nucleus, and differ only in the functional grouping attached to the side-chain.

Among various studies on histidine, subjects allied to the present work are treated in the following communications.

In 1907 Knoop⁽²⁾ reported on the oxidation reactions of histidine and its derivatives and in his study he established the constitution of this amino-acid. He oxidized imidazolyl-lactic acid $C_3H_3N_2 \cdot CH_2 \cdot CH(OH) \cdot COOH$ (I) with concentrated nitric acid and obtained imidazolyl-glyoxylic acid $C_3H_3N_2 \cdot CO \cdot COOH$ (II) which was further oxidized to imidazol-carboxylic acid $C_3H_3N_2 \cdot COOH$ (III) by the action of hydrogen peroxide in the presence of acetic acid. On the other hand, oxidation of (I) with barium permanganate yielded imidazolyl-acetic acid $C_3H_3N_2 \cdot CH_2 \cdot COOH$ (IV). He also stated that histidine $C_3H_3N_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$ itself yielded the same products (II and III) when oxidized with nitric acid, but it was not so readily attacked. In 1909 Langheld⁽³⁾ found that imidazolyl-acetaldehyde $C_3H_3N_2 \cdot CH_2 \cdot CHO$ was a reaction product when histidine hydrochloride was oxidized with sodium hypochlorite. In 1916 Dakin⁽⁴⁾ obtained cyanomethyl-imidazol $C_3H_3N_2 \cdot CH_2 \cdot CN$ by oxidizing histidine with toluene-*p*-sulphochloramide.

In none of these papers the rupture of imidazol nucleus is mentioned and no investigation is found on the electrolytic oxidation of this amino-acid.

The authors have first examined the oxidizability of histamine by the method already described⁽⁵⁾ (Fig. 1), and compared it with those compounds

(1) Y. Takayama, this Bulletin, **8** (1933), 189.

(2) Fr. Knoop, *Beitr. chem. Physiol. Pathol.*, **10** (1907), 111.

(3) K. Langheld, *Ber.*, **42** (1909), 2373.

(4) H. D. Dakin, *Biochem. J.*, **10** (1916), 319.

(5) Y. Takayama, this Bulletin, **8** (1933), 213.

previously dealt with. The curves representing the course of formation of carbon dioxide and ammonia from this amine by electrolysis are of the same type as those of imidazolyl-propionic acid and histidine. From this

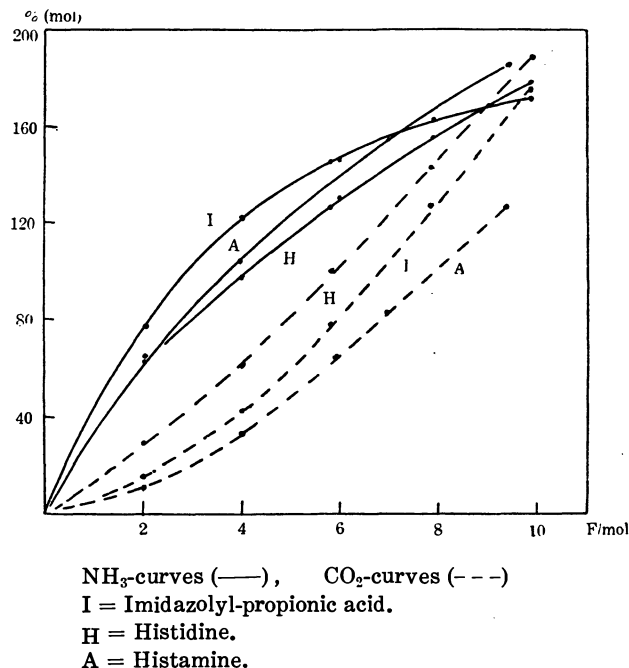


Fig. 1.

fact it can be easily expected that the courses of oxidation of these allied compounds do not show marked diversity. But they indicated obvious difference in one point, namely, in the colour of their electrolysates. The electrolysates of imidazolyl - propionic acid and histamine assumed yellowish tint as the electrolysis proceeded and never turned to black until the end while that of histidine changed to black and considerable amount of a melanin-like substance separated.

Separation of Oxidation Products of Histamine. Histamine in dilute sulphuric acid solution was electrolyzed with a lead peroxide anode and a lead cathode, conditions being similar to those in the case of imidazolyl-propionic acid, current quantity applied 6 faradays per mol, and the temperature 30°C. The electrolysate was treated with phosphotungstic acid and the precipitate (A) formed was separated from the filtrate (B).

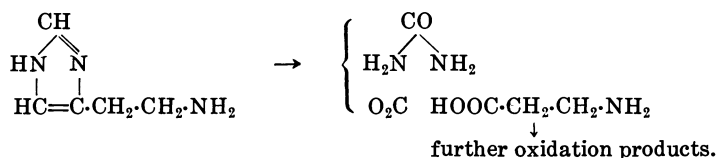
Precipitate (A). Ammonia and unchanged histamine were isolated as volatile and non-volatile bases respectively.

Filtrate (B). Urea was estimated in this part by urease method, the amount corresponding to 7.7%.* β -Alanine (8.5%) was also obtained from the concentrated solution on treatment with alcohol and ether and it was confirmed as such by converting it into α -naphthylisocyanate compound.

* Small amounts of urea (1.3%), and ammonia (1.0%) were also found in (A), thus total quantity of urea amounting to 9.3% and that of β -alanine 12.0%.

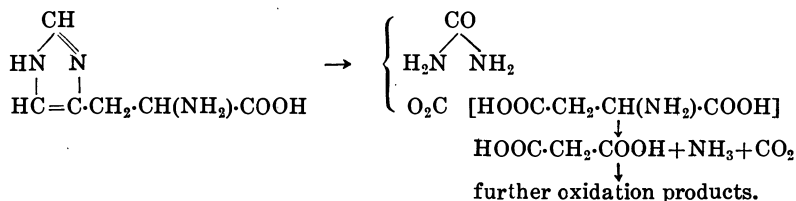
As β -alanine is said to be unstable to alkali,⁽⁶⁾ its amount can be presumed by the estimation of ammonia formed on treatment with caustic alkali. The amount of β -alanine thus found was 11.1%, under the assumption that no other substance yielding ammonia by this treatment was contained.

The Mechanism of the Reaction. The products obtained from histamine in the above oxidation comprise urea (9.0%), β -alanine (8.5% ; 12.0%), ammonia, and carbon dioxide. Considering the isolation of these substances as the basis, the course of the oxidation can be explained as follows :



Separation of Oxidation Products of Histidine. Histidine was electrolyzed just in the same manner as above. A melanin-like substance formed during electrolysis was separated after long standing and its nitrogen content was found 13.64%. The electrolysate was treated with phosphotungstic acid as usual. Ammonia and urea (11.1%) together with unchanged histidine were isolated.

Urea was obtained in each of these three cases and it would result from the rupture of imidazol nucleus, and in two previous cases succinic acid semi-aldehyde together with succinic acid and β -alanine were found respectively as the other fragments. In the case of histidine, aspartic acid was expected by analogy to be the first oxidation product, but, in point of fact, it could not be isolated. On the other hand, a small quantity of malonic acid (about 3%)⁽⁷⁾ was found, which may be assumed to be produced by the further oxidation of aspartic acid. The oxidation of histidine may be represented as follows :



(6) E. Abderhalden and A. Fodor, *Z. physiol. Chem.*, **85** (1913), 112.

(7) Malonic acid is also unstable to oxidation, hence, its poor yield. F. Lieben and E. Molnar, *Monatsh.*, **53** (1929), 7.

The electrolytic oxidation of these kindred compounds, namely, imidazolyl-propionic acid (I), histamine (II) and histidine (III) proceeded through a similar course, imidazol nucleus being attacked and yielding urea. Besides urea, (I) gave succinic acid semi-aldehyde and succinic acid, and (II) gave β -alanine, the same being the case with histidine (III). The latter gave, besides urea, aspartic acid, and this, being too unstable to remain unattacked, was completely oxidized, a part of the product remaining in its intermediate stage as malonic acid.

The formation of a melanin-like substance was restricted to one case, namely, histidine, and it may be concluded that the presence of the cyclic ring together with amino-group in the α -position to the carboxylic group is necessary for its formation.

EXPERIMENTAL PART.

Electrolytic Oxidation of Histamine. Histamine (synthesized)* which was used gave the following analytical result :

Found : N, 37.33. Calc. for $C_5H_9N_3$: N, 37.83%.

The course of formation of carbon dioxide and ammonia during electrolysis was determined after every definite consumption of electricity⁽⁸⁾ (Table 1).

Histamine (4.45g., about 40 milli-mols) was dissolved in 100 c.c. of 2N sulphuric acid and the solution was electrolyzed. Cell : without diaphragm ;

Electrodes : lead—lead peroxide (3.8 cm. $\times$ 5.5 cm.), distance 1.5 cm. ; C.D. : 2 amp./dm.² ; Electric quantity applied 6 F./mol.

Table 1.

Current quantity (F./mol)	CO ₂ /Histamine (mol %)	NH ₃ /Histamine (mol %)
1.97	9.7	60.4
3.94	34.3	102.7
5.90	67.1	130.2
6.93	82.3	154.8
9.42	126.3	182.7

The electrolysate was thoroughly extracted with ether. A small quantity of oil insoluble in water was obtained from the extract, but

its quantity was too minute for further investigation.

* The sample of histamine was kindly offered by Mr. S. Numano, to whom the authors express their thanks.

(8) Cf. Y. Takayama, this Bulletin, 8 (1933), 213.

The residue of the extraction was diluted with 5% sulphuric acid and 20% phosphotungstic acid was added to it.

Precipitate (A). It was decomposed with barium hydroxide, the solution was distilled under reduced pressure at 60°C., and the distillate was received in hydrochloric acid. The hydrochloride of the base was not hygroscopic. It was extracted with cold absolute alcohol. Bases obtained from the extract and the residue were found to be ammonia by the analysis of their platinic double chlorides.

Found for the substance from the extract: Pt, 43.16. Found for the substance from the residue: Pt, 43.72. Calc. for $(\text{NH}_4)_2\text{PtCl}_6$: Pt, 43.93%.

After removal of barium exactly, the part containing non-volatile base was concentrated under reduced pressure, but it was impossible to bring it into crystallization. The concentrated bulk was treated with picric acid and the base precipitated as picrate. It amounted to 5% and melted at 227°C. after recrystallization from water, coinciding with histamine dipicrate. No other base was obtained from the filtrate of the picrate.

Found: N, 22.28. Calc. for $\text{C}_5\text{H}_9\text{N}_3 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$: N, 22.15%.

Estimation of urea (urease method):

Solution taken: 1/20 part.* $\text{NH}_3 = 3.58 \text{ c.c. of } \text{N}/70 \text{ H}_2\text{SO}_4 = 0.0512 \text{ milli-mol.}$

Calculating into total volume, $\text{NH}_3 = 1.02 \text{ milli-mols, hence, urea} = 0.510 \text{ milli-mol (1.3\%).}$

Estimation of β -alanine (NH_3^{**} formed on heating at 100°C. for ten minutes with excess of caustic soda):

Solution taken: 1/20 part. $\text{NH}_3 = 1.46 \text{ c.c. of } \text{N}/70 \text{ H}_2\text{SO}_4 = 0.0209 \text{ milli-mol.}$

Calculating into total volume, $\text{NH}_3 = 0.42 \text{ milli-mol (1.0\%).}$

Filtrate (B). The solution, after removing barium with carbon dioxide and sulphuric acid, was concentrated to 100 c.c. by evaporation under reduced pressure. The amount of urea and β -alanine was determined.

Estimation of urea (urease method):

Solution taken: 1.00 c.c. out of 100 c.c. $\text{NH}_3 = 4.28 \text{ c.c. of } \text{N}/70 \text{ H}_2\text{SO}_4 = 0.0612 \text{ milli-mol.}$

Calculating into total volume, $\text{NH}_3 = 6.12 \text{ milli-mols, hence, urea} = 3.06 \text{ milli-mols (7.7\%).}$

Estimation of β -alanine:

Solution taken: 1.00 c.c. out of 100 c.c. $\text{NH}_3 = 3.07 \text{ c.c. of } \text{N}/70 \text{ H}_2\text{SO}_4 = 0.0439 \text{ milli-mol.}$

Calculating into total volume, $\text{NH}_3 = 4.39 \text{ milli-mols (11.0\%).}$

The remaining part of the solution was concentrated to a syrup, after decolourization with animal charcoal. The syrup was dissolved in dilute alcohol and an excess of ether was added to it until faint turbidity appeared.

* It was confirmed by the same aeration method that no trace of free ammonia was present in the solution.

** It was ascertained that histamine itself does not yield an appreciable amount of ammonia by this treatment.

The turbidity of the solution soon disappeared, an oil depositing at the bottom, which changed to crystals after long standing. The yield amounted to 0.30 g. (8.5%). The crystalline substance was dissolved in a small bulk of water and recrystallized by adding alcohol. It melted at 198–200°C. coinciding with β -alanine.⁽⁹⁾

Found: N, 16.03. Calc. for $C_3H_7O_2N$: N, 15.73%.

β -Alanine was dissolved in twice its equivalent of N NaOH, diluted with four times of water, and α -naphthyl-isocyanate (1.2 equivalents) was added to the solution. After one hour, an excess of hydrochloric acid was poured, and α -naphthyl-isocyanate compound of β -alanine precipitated. After recrystallization from alcohol it showed effervescence at 196°C. and melted completely at 226–228°C.⁽¹⁰⁾

Found: N, 11.01. Calc. for $C_{14}H_{14}O_3N_2$: N, 10.86%.

Electrolytic Oxidation of Histidine. Histidine monohydrochloride (Schuhardt) used gave the following analytical results:

Found: N, 20.04; HCl, 16.94. Calc. for $C_6H_9O_2N_3 \cdot HCl \cdot H_2O$: N, 20.05; HCl, 17.39%.

Histidine monohydrochloride (2.95 g., about 15 milli-mols) was dissolved in 100 c.c. of 2N H_2SO_4 . Sufficient water was added to the solution, and it was distilled under reduced pressure to drive off hydrochloric acid. This treatment was repeated several times until the distillate showed no trace of hydrochloric acid. The solution was made up to 100 c.c. and was electrolyzed. The current quantity applied was 8 F./mol.

The electrolysate assumed reddish tint (at 1 F./mol), then gradually changed to black, and a considerable amount of a melanin-like substance deposited on the wall of the vessel and its amount increased in the lapse of time even after the termination of electrolysis. After four months, it was separated, well washed, and analyzed after drying over quick lime. (Found: N, 13.64%.) It is amorphous black powder and readily soluble in alkali.

The electrolysate was diluted with 5% sulphuric acid and treated with phosphotungstic acid.

Precipitate (A). Ammonia was obtained as the volatile base.

Found for the chloroplatinate of the base: Pt, 43.87. Calc. for $(NH_4)_2PtCl_6$: Pt, 43.95%.

After removing barium, the part containing non-volatile base was concentrated to a small bulk. A small quantity of crystals was obtained from

(9) P. Karrer and A. Widmer, *Helvetica Chim. Acta*, **9** (1926), 888.

(10) W. Linneweh, A.W. Keil, and F.A. Hoppe-Seyler, *Z. physiol. Chem.*, **183** (1929), 17.

it, which melted at 258–260°C. with effervescence, after recrystallized from dilute alcohol. It gave positive results in ninhydrine, biuret, and *p*-diazobenzene-sulphonic acid reactions, and its hydrochloride melted at 230–231°C. The base was presumed to be unchanged histidine.

Filtrate (B). After complete separation of barium, the solution was concentrated to 50 c.c. and urea was determined.

Identification of urea (xanthydrol method):

A part of the solution was diluted with glacial acetic acid and the filtered methyl alcoholic solution of xanthydrol (Kahlbaum) was added to it. Urea was precipitated as dioxanthyl-urea.

Found: N, 6.74. Calc. for $C_{27}H_{20}O_8N_2$: N, 6.68%.

Estimation of urea (urease method):

Solution taken: 1.00 c.c. out of 50 c.c. $NH_3 = 4.67$ c.c. of $N/70 H_2SO_4 = 0.0667$ milli-mol. Calculating into total volume, $NH_3 = 3.34$ milli-mols, hence, urea = 1.67 milli-mols (11.1%).

Malonic acid: Histidine (25 milli-mols) was electrolyzed as described above. The electrolysate was thoroughly extracted with ether. After expelling ether, brown liquid was obtained from the extract and steam was passed through it to drive off volatile acid. The residue was decolourised and titrated with $N/10 NaOH$. It required 15.8 c.c., amounting to 0.79 milli-mol as a dibasic acid, which corresponds to 3.0%. The neutralized solution was concentrated and a little excess of $N BaCl_2$ was added to it. A barium salt was precipitated from it by adding 60 per cent. alcohol, which was found to be barium malonate⁽¹¹⁾ by the analysis after reprecipitation and drying at 100°C.

Found: Ba, 53.99. Calc. for $C_3H_2O_4Ba \cdot H_2O$: Ba, 53.33%.

The barium malonate obtained was dissolved in water and barium was removed as the sulphate. The crystals of the free acid were examined under polarization microscope. It showed oblique extinction, the angle of extinction being 12–13°, ⁽¹²⁾ and resembled with a pure specimens of malonic acid under the gypsum-plate.

The present work has been carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo, and the authors wish to express their sincere thanks to Prof. K. Matsubara for kind inspection of this paper.

(11) C. Coulett, *J. prak. Chem.*, **73** (1906), 76.

(12) P. Groth, "Chem. Krystallographie," III (1910), 230.

REACTIONS BETWEEN ETHYLENE CHLORIDE AND CHLORINE.

By Senzo HAMAI.

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The fact that, when ethylene and chlorine are mixed, a mixture of various chlorinated products in various proportions is formed, has been reported by several investigators.⁽¹⁾ Albert Maier⁽¹⁾ observed that when chlorine and ethylene are mixed in proportion of 2:1 at a temperature between 20° and 30°, the products are found to be 70% 1,1,2-trichlorethane, 15% ethylene chloride, 5% 1,1,2,2-tetrachlorethane, and 10% higher chlorinated products. The difficulties arising from the complex nature of the reaction implicate to the study not only theoretical but also practical importance. Mitsukuri and Kinumaki⁽²⁾ found that only ethylene chloride is formed when the experiment is carried out at low temperature. Besides, Taylor and Hildebrand⁽³⁾ published a paper on the solubility of chlorine in ethylene bromide, a compound similar to ethylene chloride, and it was conventionally considered that there was no reaction between chlorine and ethylene chloride; but the evidences so far obtained by the present author definitely show that there are reactions between chlorine and ethylene chloride.

In view of these facts, the study of the reactions of chlorine with ethylene chloride would be very much interesting for clarifying the nature of chlorination of hydrocarbons. Although the work is not yet completed, the purpose of this paper is to point out some of important facts so far found along with some suggestions for the future work.

Materials. Ethylene chloride, from Takeda (b.p. 83.0°), after treated with phosphorus pentoxide and calcium chloride, was subjected to fractional distillation several times, and only the middle portions were used (refractive index 1.44240⁽⁴⁾ for H_x-line at 25°).

Chlorine, vaporized from ordinary commercial liquid chlorine in cylinder, was passed through water, concentrated sulphuric acid, and a phosphorus pentoxide tube, condensed by cooling with liquid air or liquid nitrogen, and

(1) A. Maier, German Patent, 522959, Aug. 26, 1926; Stewart and Smith, *J. Am. Chem. Soc.*, **51** (1929), 3091; P. Askenasy and A. Hieler, German Patent, 549341, May 13, 1930.

(2) Mitsukuri and Kinumaki, *J. Chem. Soc. Japan*, **53** (1932), 398.

(3) Taylor and Hildebrand, *J. Am. Chem. Soc.*, **45** (1923), 682.

(4) S. Hamai, This Bulletin, **8** (1933), 297.

vaporized again. This process was repeated three times, the initial and the last portions being rejected each time.

Reaction of Chlorine and Liquid Ethylene Chloride. Chlorine was passed into ethylene chloride in the reaction chamber as shown in Fig. 1. The three ends of the inlet tube A are covered with platinum foils, each with a fine hole, so as to form very minute bubbles of chlorine in ethylene

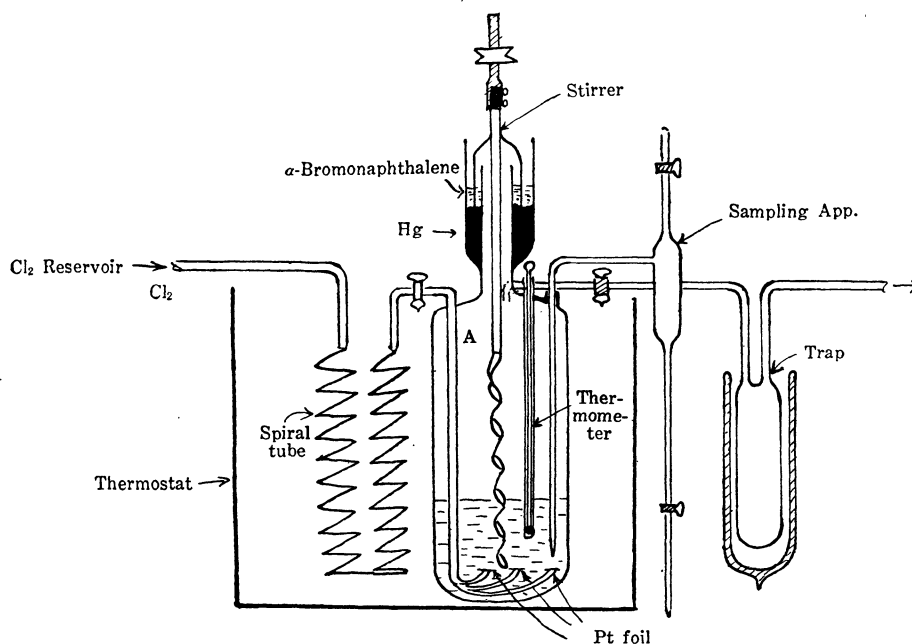


Fig. 1.

chloride. Chlorine was passed for various lengths of time, from 2 to 5 hours, at 50°. The whole reaction vessel was kept in a thermostat, rape-seed oil being used as the thermostat liquid. The rate of flow of chlorine was adjusted to 125–250 c.c. per minute. After a certain time the solution was taken out, washed with sodium hydroxide, dried with calcium chloride, and subjected to fractional distillation. No trace of expected substitution products was obtained. Similar experiments were carried out at 25° and 30°, and chlorine was passed for 2–5 hours with and without radiation by a mercury lamp at both temperatures.

In no case, on treating the mixture as mentioned above, any compound of higher boiling point than ethylene chloride was found; however at the outside of the chamber, in the tube where possibly ethylene chloride vapour

diffused when chlorine was led into the liquid by opening the stopcock, and in one of the traps attached directly to the reaction chamber, the formation of a white crystalline substance was observed after a long while. It was found to be hexachlorethane by its odour somewhat like camphor and m.p. 185°.

In another experiment ethylene chloride was mixed with about one fourth its volume of carbon tetrachloride, and the reaction was carried out under radiation by a mercury lamp.⁽⁵⁾ On the following day a crystalline substance was noticed on the wall of the chamber after the solution was taken out, and also the crystals were found, as in the previous case, in the chlorine trap which is attached to the spiral tube of the inlet just outside the thermostat (not shown in the figure).

Correlating with other evidences from previous experiments, this fact possibly means that higher chlorinated derivatives may be formed only where the concentration of chlorine is high and the partial vapour pressure of ethylene chloride is relatively low. This is also concordant with the facts which will be discussed later. Formation of hydrogen chloride is also noticed; this is just as much concordant with the fact that platinum foils used at the ends of the inlet tube was found corroded, for chlorine alone can not possibly corrode platinum, but can with hydrogen chloride. Therefore, the fact that it was unable to find any trace of substituted compounds when the substitution of chlorine for hydrogen in ethylene chloride was tried is probably due to the reasons: (1) the substitution is so slow that on passing chlorine the reaction is not very appreciable, and (2) the substituted amount is too small to be detected by fractional distillation.

In order to see the effect of hydrogen chloride on the reaction, chlorine alone was passed into pure ethylene chloride in one vessel, and in the other, chlorine was passed into ethylene chloride mixed with hydrogen chloride gas, and both were allowed to stand for several hours. Ethylene chloride containing hydrogen chloride decolorized chlorine much faster than that without hydrogen chloride gas. This apparently shows that hydrogen chloride acts as a catalyst in chlorination of ethylene chloride. On fractional distillation, it was found that 1,1,2-trichlorethane was formed (b.p. 113.5°, the refractive index 1.47345⁽⁶⁾ for H_α-line at 25°). In the previously mentioned experiments (flow method), no substituted compound was found except C₂Cl₆ formed in the vapour phase. However, definite evidences of substitution were obtained when the static method was employed. Ethylene

(5) Effect of mercury lamp radiation may not be found so much noticeable unless more precise measurement is carried out.

(6) Unpublished data.

chloride was put in the vessel as shown in Fig. 2, the system was evacuated, and chlorine was passed in by opening the stopcock A, which was then closed. The temperature measured outside the vessel rose in one case from 16° to 21° , and in other cases, from 16.75° to 22.75° and from 17° to 47° .

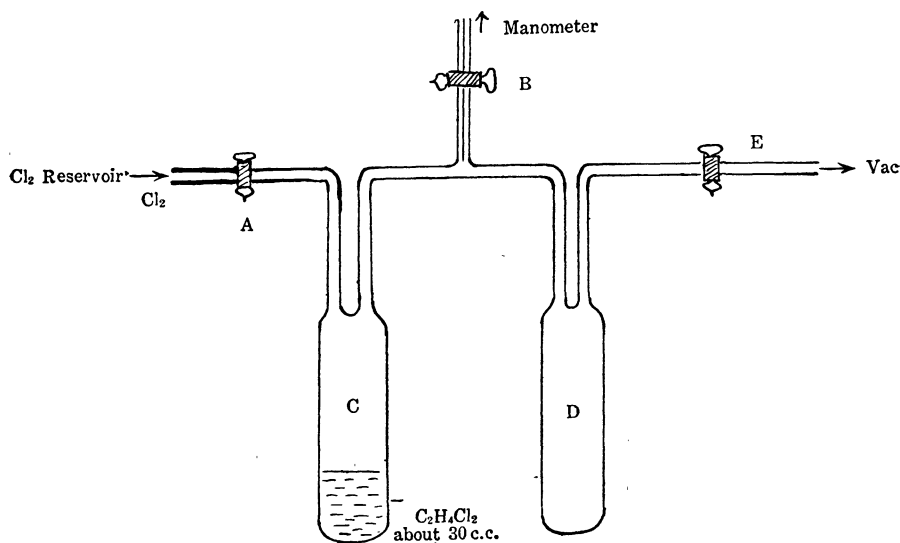


Fig. 2.

Moreover, the mercury- α -bromonaphthalene manometer indicated the rise of pressure from 14.35 cm. to 189.0 cm. at 17° , and from 76.0 cm. to 126.0 cm. at 18° .

At first the reaction is very slow, but after a certain time it becomes appreciable and gradually faster, showing a possible existence of an induction period. More experiments have been carried out and although they are not strictly quantitative, all of them have shown that chlorine, though slowly, reacts with ethylene chloride with the rise of temperature and increase of pressure. The increase of pressure is possibly due to the difference in solubilities of chlorine and hydrogen chloride in ethylene chloride. (Absorption of hydrogen chloride by ethylene chloride is now under investigation. The solubility of hydrogen chloride is much smaller than that of chlorine. The details will be published soon.) Hexachlorethane was noticed on the walls particularly at part D in Fig. 2 agreeing to the evidences found in the previous cases, and from the liquid part merely trichlorethane was obtained by fractional distillation. The formation of trichlorethane on mixing chlorine with ethylene chloride was demonstrated

again in the attempt⁽⁷⁾ of measuring the solubility of chlorine in ethylene chloride; in this attempt no concordant results for the solubility were observed owing to the reaction between them.

Stewart and Smith⁽⁸⁾ in the experiment of the reaction between ethylene and chlorine observed that, as soon as liquid ethylene chloride was formed on the wall of the reaction vessel, the rate of reaction became faster corresponding to the so-called induced substitution as caused by energy given out by excited ethylene chloride molecules, and they found trichlorethane and hydrogen chloride but no other higher chlorinated compounds. But the fact that ethylene chloride reacts with chlorine shows that trichloroethane formation is not necessarily be induced by addition reaction as suggested by Stewart and Smith. It can be independent, and furthermore, energy necessary for substitution can be supplied from other sources such as collision or possible excitation of chlorine to higher quantum states (Energy of excited chlorine as found from the spectral data is 0.233 volt⁽⁹⁾ (heat of dissociation)).

Reaction Between Ethylene Chloride Vapour and Chlorine. In order to study the nature of the gaseous reaction between ethylene chloride and chlorine the following scheme has been carried out.

The reaction chamber was connected to the ethylene chloride reservoir and after allowing its vapour into the chamber, the stopcock was closed, the pressure of ethylene chloride vapour being maintained slightly lower than the saturated vapour pressure.

Table 1.

Tem. (°C.)	$\frac{P_{Cl_2}}{P_{C_2H_4Cl_2}}$	Time (hrs.)
35	4.5	3
35	3	1/2
35	4	3
25	2.3	4
25	5	2½
25	2.3	3

The vapour was mixed with chlorine by opening the stopcock and after closing it the mixture was left for various lengths of time at various temperatures, the whole vessel being immersed in the thermostat. The experiments were carried out with mixtures in various proportions (Table 1).

The gaseous mixture was then condensed by cooling with liquid air or liquid nitrogen. It was found, however, that the reaction is extremely slow, and

(7) Discordant results have been found in several experiments of measuring the solubility of chlorine in ethylene chloride by a procedure somewhat similar to Taylor and Hildebrand's for measuring the solubility of chlorine in ethylene bromide, *J. Am. Chem. Soc.*, **45** (1923), 682.

(8) Stewart and Smith, *J. Am. Chem. Soc.*, **52** (1930), 2869; **51** (1929), 8091.

(9) International Critical Table, Vol. 5.

where chlorine is largely in excess hexachlorethane formation predominates in the gaseous phase and no other reaction is appreciable, while in the reaction between liquid ethylene chloride and chlorine there occurs trichlorethane formation especially on the surface (liquid-vapour interface) as semiquantitatively observed by the rise of temperature along the liquid-gas interface. This fact is concordant with the theoretical consideration that on the interface the concentration of chlorine is much higher than inside the body of ethylene chloride into which chlorine has been dissolved, favouring naturally the substitution reaction by chlorine.

Thus some important facts about the reactions between chlorine and ethylene chloride both in liquid and vapour phases have been pointed out, although they are not based strictly on quantitative data because of the complex nature of the reactions as well as lack of a suitable method of measurement. It is hoped that a more detailed study will be reported some time.

Some Suggestions for the Future Work. There are several investigators⁽¹⁰⁾ who have studied infra-red absorption bands which are attributed to the carbon-hydrogen linkage in carbon hydrogen compounds as well as in their chlorine derivatives; furthermore Smith and Board⁽¹¹⁾ observed that substitution of chlorine for hydrogen in tetrachlorethane causes a remarkable decrease in the intensity of absorption in each of the characteristic absorption bands without any evident shift of its position, and a similar phenomenon takes place in the transformation from dichlorethylene to trichlorethylene. Such compounds as carbon disulphide and carbon tetrachloride have no such bands. Smith and Board⁽¹¹⁾ also state that the intensity is approximately a direct function of the number of hydrogen-carbon linkages. Later Spence and Easley⁽¹²⁾ studied more carefully infra-red absorption bands of halogen derivatives of ethane, some fourteen compounds including the series of $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5 and C_2Cl_6 , and found that, as concluded by several previous investigators already, the mentioned absorption bands are due to carbon-hydrogen linkages, the intensity of absorption is a function of the number of C-H-linkages, and the bands completely vanish in hexachlorethane as in the case of carbon tetrachloride.

Looking over these papers, it is rather interesting to notice that the intensity of absorption decreases with chlorine substitution without shift of

(10) Ellis, *Phys. Rev.*, (2), **23** (1924), 48; *J. Opt. Soc. Am.* **8** (1924), 1; Coblentz, *Bur. Stand. Sci. Paper*, No. 148 (1921).

(11) Smith and Board, *J. Am. Chem. Soc.*, **48** (1926), 1512.

(12) B. J. Spence and M. A. Easley, *Phy. Rev.*, **34** (1929), 730.

the positions of bands, and that might be an available method for the study of chemical reactions in which chlorine substitution occurs and for which the ordinary conventional method of attack is not suitable, when the reaction is rather slow. Making use of the infra-red absorption phenomena we might be able to investigate chemical reactions which otherwise could not be easily studied. Whether it is practically useful or not must be decided by actual experiments.

Summary.

(1) In the reaction between chlorine and ethylene chloride in the liquid phase 1,1,2-trichlorethane is the principal product and in the gaseous phase the formation of hexachlorethane predominates.

(2) The reaction between gaseous chlorine and liquid ethylene chloride seems to occur mainly on the liquid gas interface.

(3) Hydrogen chloride gas dissolved in the mixture catalytically accelerates the reaction.

(4) There seems to exist an induction period in the reaction between ethylene chloride and chlorine possibly owing to catalytic acceleration by either hydrogen chloride or substituted product or both in later stage.

(5) In the gaseous reaction between chlorine and ethylene chloride the formation of hexachlorethane predominates especially when chlorine exists largely in excess to ethylene chloride vapour.

(6) A suggestion is made as to the method of study on chemical reactions, especially on chlorination reaction (substitution).

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