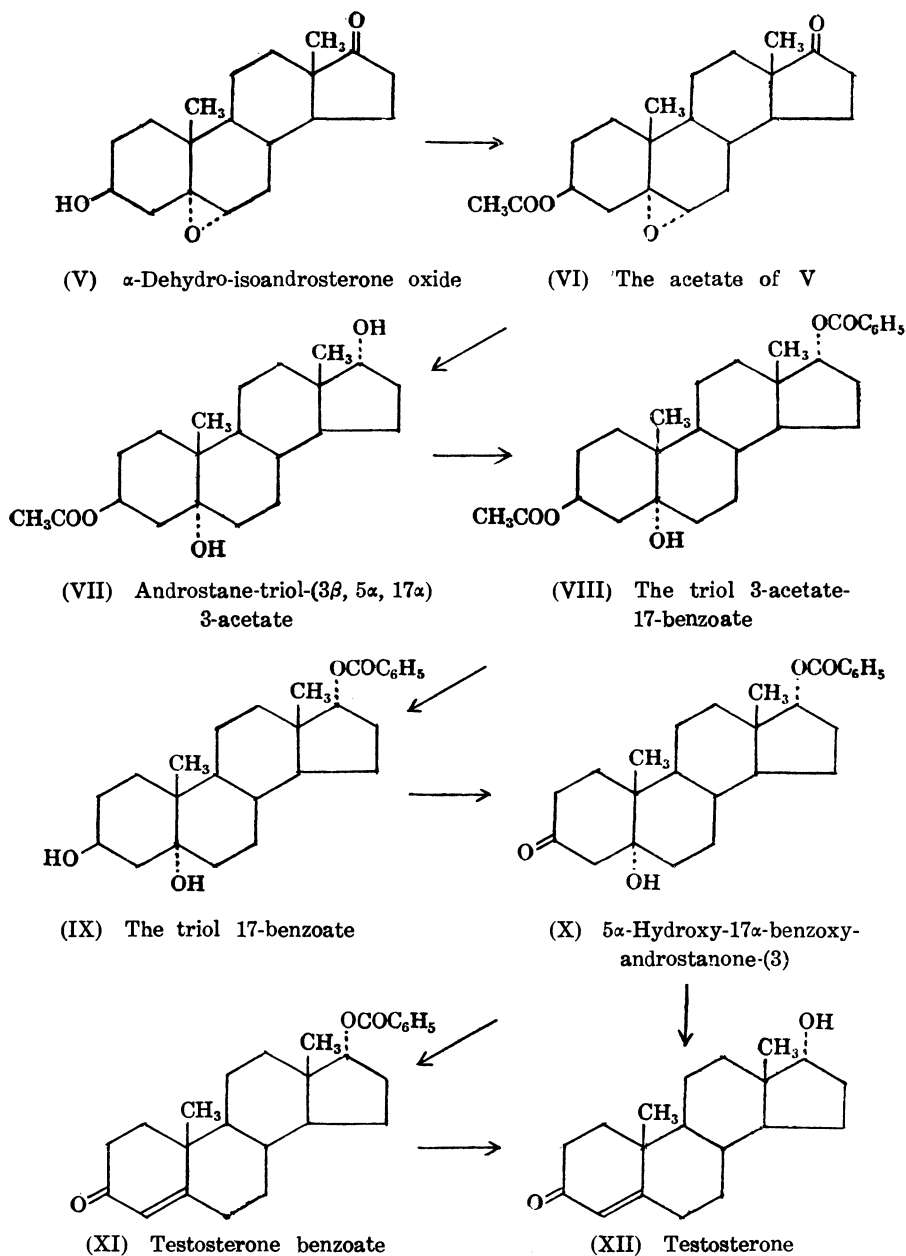


compared with those obtained with cholesterol oxide acetates⁽⁴⁾. Their configurations, however, had not yet been determined inasmuch as the designations α and β had been arbitrary in cholesterol oxides. α -Dehydro-isoandrosterone oxide acetate gave the changes corresponding to those of α -cholesterol oxide acetate, as described below, and thus was found to



(4) M. Ehrenstein, *J. Org. Chem.*, **6** (1941), 626. For earlier literature cf. *loc. cit.*

possess the same α -oxido structure (VI) as the latter, the configuration of which had been determined by one of the authors as mentioned above.

Catalytic reduction of α -dehydro-isoandrosterone oxide acetate (VI) (m. p. $220\sim221^\circ$), prepared from α -dehydro-isoandrosterone oxide (V) (m. p. $224\sim225^\circ$) with acetic anhydride and pyridine, with platinum oxide in glacial acetic acid gave androstane-triol-($3\beta,5\alpha,17\alpha$) 3-acetate (VII), plates melting at $200\sim202^\circ$ from acetone or ethyl acetate. On the reduction the oxido ring was splitted at the side of carbon atom 6 as in α -cholesterol oxide acetate⁽⁵⁾ and the carbonyl group at carbon atom 17 was reduced to a hydroxyl group at the same time. The α - or trans-configuration of this hydroxyl group was determined because the triol finally gave (trans-)testosterone as described below.

The triol 3-acetate was benzoylated with benzoyl chloride and pyridine to androstane-triol-($3\beta,5\alpha,17\alpha$) 3-acetate-17-benzoate (VIII), prisms melting at $232\sim234^\circ$ from alcohol or ethyl acetate. Partial saponification with a calculated amount of methanol potash in two portions at the room temperature gave then androstane-triol-($3\beta,5\alpha,17\alpha$) 17-benzoate (IX), flat needles or plates melting at $254\sim256^\circ$ from acetone. Oxidation of the latter with chromic acid in glacial acetic acid at the room temperature yielded 5α -hydroxy-17 α -benzoxy-androstanone-(3) (X), scales melting at $230\sim232^\circ$ from alcohol, which was dehydrated with thionyl chloride and pyridine or better with hydrogen chloride in chloroform to testosterone benzoate (XI) melting at $180\sim182^\circ$. Saponification of the benzoate with methanol potash gave testosterone (XII) melting at $152\sim153^\circ$. The substance thus obtained was identified with an authentic specimen in the free state and in the form of acetate.

The action of dilute methanol potash on 5α -hydroxy-17 α -benzoxy-androstanone-(3) effected saponification and dehydration to testosterone in one procedure.⁽⁶⁾

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(5) By a similar catalytic reduction the oxido ring in β -cholesterol oxide acetate is splitted at the side of carbon atom 5 and cholestane-diol-($3\beta,6\beta$) 3-acetate (but none of coprostane derivatives) is formed.

(6) Japanese Patent applied for on March 20th, 1947. This improvement was not reported in the paper read before the annual meeting mentioned above but included in the doctor thesis by M. Chuman.

Über die intramolekularen Umlagerung des δ, δ -Diäthyl- γ -amino- δ -valerolactons.*

von Seizo KANAO.

(Eingegangen am 20. Mai 1945.)

Es wurde früher⁽¹⁾ vom Verfasser festgestellt, dass beim Grignardieren des α -Aminoglutar säure-diäthylesters kein Aminoglykol wie beim Asparaginsäure-diäthylester⁽²⁾ entstand, sondern unter Ringschluss [α -Pyrrolidonyl-(α')]-diäthylcarbinol lieferte. Auf diese Weise erhielt Verfasser nicht nur Dialkyl-, Diaryl- bzw. Dialphyl-carbinol in der Pyrrolidonreihe, sondern auch die entsprechende in der Piperidonreihe aus dem α -Aminoadipinsäure-diäthylester. Insbesondere stellt [α -Pyrrolidonyl-(α')]-diäthylcarbinol (I) sehr schwach basische Prismen vom Schmp. 91–92° dar, die durch soda-alkalische 3, 5-Dinitrobenzoesäure kirschrot färben.

Durch Verseifen mit Barytlauge ging dieser Carbinol in eine δ, δ -Diäthyl- δ -oxy- γ -amino- n -valeriansäure (II) in fast quantitativer Ausbeute über, wobei sich solche Oxyaminosäure als prachtvolle Prismen vom Schmp. 143° abschied, die in wässriger Lösung die Polarisations ebene nach links, dagegen in salzsaurer Lösung nach rechts dreht. Sie wurde von ihrer β -Naphthalinsulfo-verbindung noch näher charakterisiert.

Leitete man trockenes Chlorwasserstoffgas in absolut alkoholischer Lösung der obigen Oxyaminosäure ein, so verwandelte sie unter Austritt von 1 Mol. Wasser in das δ, δ -Diäthyl- γ -amino- δ -valerolacton (III), das sich als krystallinisches Chlorhydrat vom Schmp. 209° gewonnen lies. Das freie Aminolacton stellt ein basisch riechendes Öl, k_p ₁₀ 126–127°, dar, welches bei Zimmertemperatur haltbar, aber in der Wärme nicht stabil ist; beim Vakuum-Erhitzen wandelte das Aminolacton grösstenteils in das erheblich hochsiedende Destillat (k_p ₁₂ 210–211°) um, das allmählich in sehr schwach basischen Krystallen erstarrte und die positive 3,5-Dinitrobenzoesäure-Reaktion gab; ausserdem erwies sich das letzte Umwandlungsprodukt in all den Eigenschaften mit dem [α -Pyrrolidonyl-(α')]-diäthylcarbinol als identisch.

Auf Grund dieser Ergebnisse lässt sich daran bemerken, dass das Aminolacton durch Atomverschiebung eines in Aminogruppe vorhandenen Wasserstoffs nach benachbartem Lacton-Oxy in ein neues Lactam, nämlich Pyrrolidonderivat, übergegangen worden ist, und damit die genannte Umlagerung intramolekular stattfand. So ist die Beobachtung von E.

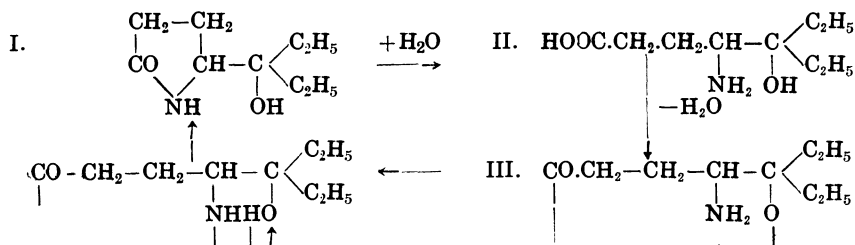
* Über die Umlagerung der Aminosäure u. ihrer Verwandten, VI. Mitteilung.

(1) *J. Pharm. Soc. Japan*, **48** (1928), 41; *Chem. Zentr.*, 1928, II, 50.

(2) C. Paal u. E. Weidenkaff, *Ber.*, **39** (1906), 4344.

Fischer und H. Leuchs⁽³⁾, ein Beispiel, dass das freie α -Amino- γ -valerolacton sich schon bei Zimmertemperatur unter Polymerisierung in Di- β -oxypropyl-diketopiperazin verwandelt; man könnte wenigstens daran denken, dass das δ,δ -Diäthyl- γ -amino- δ -valerolacton in freiem Zustande thermolabil ist.

Schliesslich möchte ich noch darauf hinweisen, dass die oben geschilderte Oxyaminosäure, die zuerst aus dem $[\alpha$ -Pyrrolidonyl-(α')]-diäthylcarbinol geht, über Aminolacton unter ringschliessende Umlagerung in den $[\alpha$ -Pyrrolidonyl-(α')]-diäthylcarbinol zurückkehrt, diese kreislaufende Umwandlung wohl als das folgende Schema aufzufassen ist:



Beschreibung der Versuche.

$[\alpha$ -Pyrrolidonyl-(α')]-diäthylcarbinol (I).

In einer Lösung aus 14.4 g. Magnesium, 65.7 g. Äthylbromid und mässigem absol. Äther wurden 20.3 g. *l* (+)-Glutaminsäure-diäthylester oder 15.7 g. *l* (–)-Pyrrolidoncarbonsäure-äthylester unter Kühlung allmählich zugegeben und auf den Wasserbade anderthalbe Stunde erwärmt. Das Reaktionsprodukt wurde mit Eis und berechneter Menge Phosphorsäure behandelt und Ammoniakwasser in die vom Äther abgetrennte sauren Lösung unter Erwärmen zugegeben. Die vom Ammoniummagnesiumphosphat abfiltrierte Lösung wurde im Vakuum eingeeengt und ätzkalisch erschöpfend ausgeäthert. Der ätherische Auszug wurde über Natriumsulfat getrocknet und den Äther abdestilliert und der hinterbleibende Rückstand im Vakuum destilliert, wobei er fast alle unter 13 mm. bei 211° überging. Beim Umdestillieren gibt er $\text{kp. } 206^\circ$. Das zähe Destillat wurde dreimal aus Äther zu 9 bis 10 g. farblosen, langen Prismen krystallisiert. Der Körper schmilzt bei $91\text{--}92^\circ$.

Der spezif. Drehwert:

$$[\alpha]_D^{25} = -0.52 \times 18.4500/2 \times 1.0048 \times 0.6810 = -7.01 \text{ (in Wasser).}$$

Er löst sich leicht in Wasser, Alkohol, ziemlich in Äther, schwer in Petroläther. Aus der wässrigen Lösung scheidet er als Öl durch festem

(3) Ber., 35 (1902), 3799.

Kaliumcarbonat aus. Beim Erwärmen mit 3,5-Dinitrobenzoesäure in Sodalösung färbt er kirschrot. Durch alkalische Kupferlösung (2% CuSO_4 u. 20% Natronlauge) zeigt er zuerst keine Veränderung, aber nach einiger Stunden schlägt er in purpur-blaue Farbe um, die von langsamer Ausbildung einer unten beschriebenen Oxyaminosäure verursacht ist.

δ,δ -Diäthyl- δ -oxy- γ -amino-*n*-valeriansäure (II).

17.1 g. [α -Pyrrolidonyl-(α')]-diäthylcarbinol wurden mit 20%iger Barytlauge (40 g. Bariumhydroxyd) drei Stunden unter Rückfluss gekocht. Dann wurde mit Wasser auf einem Liter verdünnt und das Barium aus der heissen Lösung durch Einleiten von Kohlensäure gefällt. Aus dem Filtrat wurden die letzte Reste des Bariums mit weniger verd. Schwefelsäure entfernt und die Lösung im Vakuum verdampft. Man löst die hinterbleibende Krystalle aus Wasser zu farblosen kurzen Prismen um. Die Ausbeute beträgt fast quantitativ.

Die Säure schmilzt blasig bei 143° . Sie ist leicht löslich in Wasser, Alkohol. Die Lösung reagiert sauer und schmeckt bitter. Durch alkalische Kupferlösung gibt sie sofort purpurne Kupferverbindung, die in Wasser leicht löslich ist. Die Ninhydrin-Reaktion ist auch positiv.

$\text{C}_9\text{H}_{19}\text{O}_3\text{N}$ (189.16) Ber. N, 7.41. Gef. N, 7.53.

$[\alpha]_D^{20} = +3.36^\circ$ (in Wasser); $[\alpha]_D^{20} = -14.48^\circ$ (in 0.3 N-Salzsäure).⁽⁴⁾

β -Naphthalinsulfo-Verbindung der δ,δ -Diäthyl- δ -oxy- γ -amino-*n*-valeriansäure, $(\text{C}_2\text{H}_5)_2\text{C}(\text{OH})-\text{CH}(\text{NH}\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_7)-\text{CH}_2-\text{CH}_2-\text{COOH}$.

Nach der Vorschrift von E. Fischer und P. Bergell⁽⁵⁾ wurden 0.5 g. der Oxyaminosäure mit 10.5 c.c. N-Natronlauge (4 Mol.), 1 g. β -Naphthalinsulfochlorid in 15 c.c. Äther tüchtig geschüttelt, die von ätherische Schicht abgetrennte und filtrierte alkalische Lösung mit Salzsäure unter Kühlung angesäuert. Nach 3 stdg. Stehen in der Kälte wurden die Krystalle abgesaugt, die erst aus verd. Methanol und dann aus Methanol umgelöst wurden. Die Ausbeute beträgt annähernd quantitativ. Rhombische Prismen vom Schmp. 203° (unter Aufschäumen). In Alkohol, Aceton und heissem Methanol löslich. Die Verbindung ist langsam löslich in Kaliumbicarbonatlösung und gegen Lackmus schwach sauer.

$\text{C}_{19}\text{H}_{25}\text{O}_5\text{NS}$ (379.28) Ber. C, 60.11; H, 6.55; N, 3.69; S, 8.45.

Gef. C, 60.12; H, 6.81; N, 3.86; S, 8.19.

δ,δ -Diäthyl- γ -amino- δ -valerolacton (III).

(4) *J. Pharm. Soc. Japan*, **48** (1928), 357.

(5) *Ber.*, **35** (1902), 3779.

5 g. δ,δ -Diäthyl- δ -oxy- γ -amino- n -valeriansäure wurden in 30 c.c. absolutem Alkohol gelöst und durch Einleiten von trockenem Chlorwasserstoffgas gesättigt und darauffolgend auf dem Wasserbade eine halbe Stunde erwärmt. Dann wurde sie im Vakuum verdampft und der syrupösen Rückstand mit Äther über Nacht stehen gelassen, wobei es Krystallmasse lieferte, die man abfiltrierte und mit alkoholhaltigem Äther (1:9) nachwusch. Man löste sie aus Aceton-Äther zu weissen Nadeln um. Das Derivat schmilzt bei 209° . Es ist leicht löslich in Wasser, Alkohol. Die wässrige Lösung gibt durch alkalische Kupferlösung keine Farbreaktion, aber durch Ninhydrin zeigt sie eine rötliche Färbung.

$C_9H_{17}O_2N \cdot HCl$ (207.61) Ber. C, 52.02; H, 8.25; N, 6.74; Cl, 17.07.

Gef. C, 51.71; H, 8.46; N, 6.60; Cl, 17.27.

$[\alpha]_D^{25} = -0.05^\circ \times 5.1403 / 1 \times 1.011 \times 0.1577 = -1.61^\circ$ (in Wasser).

Freies Aminolacton: Das oben erwähnte Chlorhydrat wurde möglichst im geringen Wasser gelöst und unter Eiskühlung mit konz. Kaliumcarbonatlösung versetzt und öfters ausgeäthert, die über wasserfreies Natriumsulfat getrocknete ätherische Lösung möglichst rasch im Vakuum destilliert, wobei es unter 10 mm. Druck bei $126-127^\circ$ siedete und die Hauptmenge in Pyrrolidonderivat verwandelt wurde.

Umlagerung von δ,δ -Diäthyl- γ -amino- δ -valerolacton.

Wurde diese Aminolacton langsam in Vakuum destilliert, so stieg die Temperatur auf und destillierte nach einiger stossartigen Erscheinung konstant unter 13 mm. Druck bei $210-211^\circ$ aus. Das zähe Destillat wurde zweimal aus Äther zu Prismen krystallisiert, die den Schmp. $91-92^\circ$ zeigten. Sie zeigten die 3,5-Dinitrobenzoesäure-Reaktion dagegen keine alkalische Kupferlösung-Reaktion mehr. Die Mischprobe mit dem oben erwähnten $[\alpha$ -Pyrrolidonyl-(α')]-diäthylcarbinol gab keine Depression. Der Analysen- sowie Drehwert stimmt auch mit dem Wert des letzten überein.

$C_9H_{17}O_2N$ (171.14) Ber. C, 63.10, H, 10.01; N 8.19.

Gef. C, 63.09, H, 10.06; N 8.28.

$[\alpha]_D^{20} = -0.47^\circ \times 18.4476 / 2 \times 1.0042 \times 0.6077 = -7.10^\circ$ (in Wasser).

Aus dem wissenschaftlichen Laboratorium von Dainippon-Kagakukogyokaisha (Gross-Japanisch Chem. Industrielle Aktiengesellschaft).

On the Configuration of Chain Molecules. II.

The effect of intramolecular interaction on the apparent volume of the flexible long-chain molecule.*

By Keizō SUZUKI.

(Received July 15, 1948.)

1. The standard state.

The configuration of the long chain molecule is a very important factor deciding the physical properties of its solution such as viscosity, diffusion, sedimentation velocity, etc.

If the parts of the chain have the tendency to bend irregularly, the long chain shows various configurations like the traces of a Brownian particle. The distance r of the both ends of such a molecule has the mean value

$$\langle r^2 \rangle = b^2 a^2 n \quad (1)$$

where a is the length of an element of the chain, n is the number of the elements, and b is the constant showing flexibility. The value b^2 is 1 for the independently flexible elements, 2 for the free rotation model of paraffine, and about 6 for the hindered rotation model of it. The distribution probability of r is also known, but r expresses insufficiently the degree of 3-dimensional extension of the molecule. (Fig. 1).

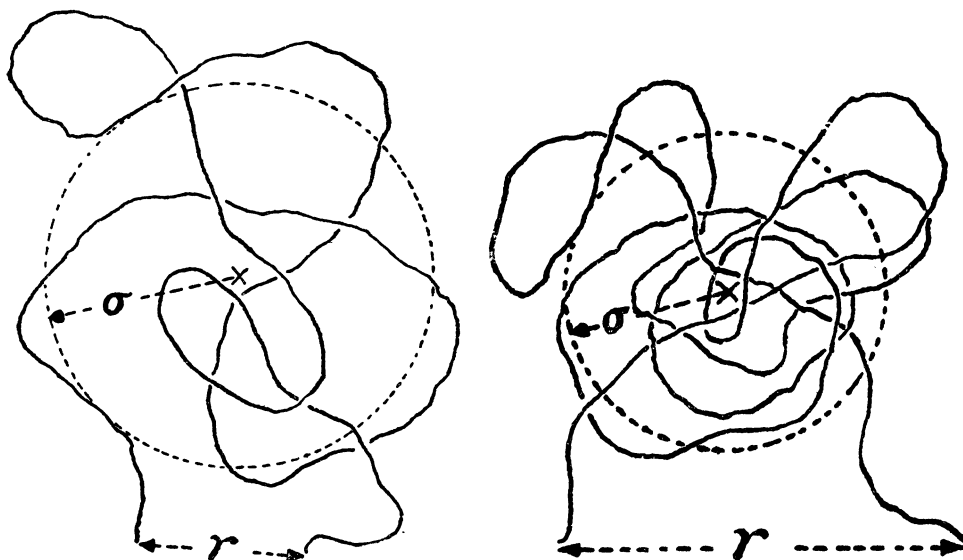


Fig. 1. The length r and the radius σ .

* Read in the annual meeting of the Society on Apr. 3, 1948.

Next, we take up 'the radius of gyration' for this purpose. Let $r_1, r_2, \dots, r_i, \dots$ be the distances of elements from the centre of mass, σ is defined by the formula

$$\sum r_i^2 = 3n\sigma^2 \quad (2)$$

The mean square value of the radius of gyration of ordinary use around the axis through the centre of mass is equal to $2n\sigma^2$. σ_0 , the square root of the mean value of the square of σ , for the molecule above shown, is given by the equation

$$\sigma_0^2 = \langle \sigma^2 \rangle = \langle r^2 \rangle / 18^{(1)(2)} \quad (3)$$

and the distribution of σ is in the similar type to that of r :

$$A\sigma^2 \exp(-\alpha\sigma^2)d\sigma, \text{ where } A = 4\sqrt{\alpha^3/\pi}, \alpha = 3/2\sigma_0^2 = 27/b^2a^2n \quad (4)$$

The state in which equations (1), (3) and (4) are correct is now named as the standard state.

2. The solvation energy.

These properties of the standard state have been derived on the assumption that there are no forces between the elements of the chain apart from each other on the chain. But however apart along the chain the elements near enough in the space can affect each other. If the energy of contact of the element is high, the molecule is apt to take the more extended configurations, and if low, the less extended. We shall discuss the effect of this energy on average values of σ , the quantity expressing the apparent volume of the molecule.

If the chain molecule is surrounded by other molecule of the same species, for example one of the isoprene polymers in rubber block, many of the elements of the chain may have no contact with any other elements of 'this' molecule, but must always be in contact with some other elements of 'other' molecules of the 'same' nature. Therefore the energy is independent of the contact of two parts of a molecule, and the ideal equations (1), (3) and (4) are correct. The condition is similar in the case where the surrounding molecules are separated into shorter chains. Thus we can say that there is no effect of the intramolecular attraction or repulsion in the solvents of the homologous series of the chain molecule, e. g. polyethylene in the solvents of paraffine series.

In other solvents the contacts are accompanied by some excess of energy, positive or negative. And the distribution is dominant in the

(1) K. Suzuki, this Bulletin, **20** (1947), 19.

(2) P. Debye, *J. Chem. Phys.*, **14** (1946), 636.

states of lower energy than those of higher energy, and the averages of σ will differ from those of the standard state.

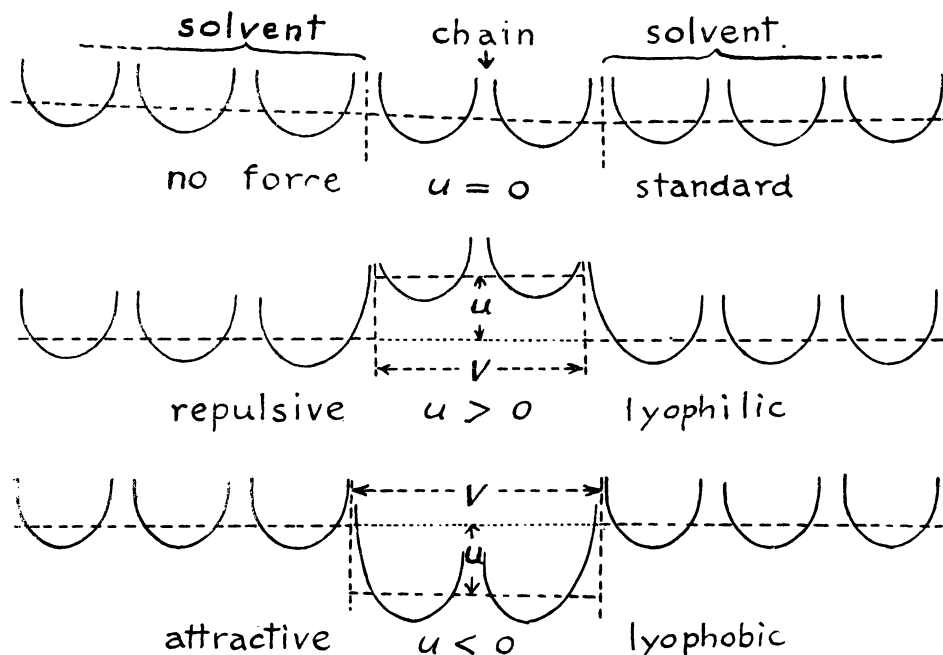


Fig. 2. Potential energy of an element of the chain in the neighbourhood of another element. u : contact energy. v : contact range.

The difference of energy due to the removal from the molecules of the same kind and the contact with solvent molecules is called 'solvation energy' and is the important factor which decides the apparent volume.

3. Contact number.

If an element is in the small volume v in the neighbourhood of another element, we consider that these elements are in contact with each other and have excess energy u compared with other two elements which are apart from each other and surrounded by solvent molecules.

The number of contacts f of this kind within a molecule must be given by the formula

$$f \propto v n^2 \sigma^{-3}$$

This proportional constant is estimated as follows: the distribution probability of an element of a molecule of the given σ in the volume element $dx dy dz$ in the Cartesian coordinate system with the origin at the centre of mass is

$$p dx dy dz = (\sqrt{2\pi}\sigma)^{-3} \exp \{-(x^2 + y^2 + z^2)/2\sigma^2\} dx dy dz \quad (5)$$

The probability that another element is in the small volume v in the neighbourhood of the first is pv . The number of combinations of two elements is $n^2/2$. Then we can calculate the contact number by integration of the product of these three factors

$$f = \iiint p^2 v n^2 / 2 \, dx dy dz$$

and we get

$$f = v n^2 \sigma^{-3} / 16 \pi^{1.5} \quad (6)$$

The total excess energy U must be

$$U = fu = v u n^2 \sigma^{-3} / 16 \pi^{1.5} \quad (7)$$

If there are various degrees of contact, and the values of energy are u_1 in the range v_1 , u_2 in the range v_2 , etc., then U must be

$$U = (v_1 u_1 + v_2 u_2 + \dots) n^2 \sigma^{-3} / 16 \pi^{1.5} \quad (7a)$$

The equation (7) includes the eq. (7a), if we consider that

$$vu = v_1 u_1 + v_2 u_2 + \dots$$

4. The corrected mean of σ approximation.

The distribution of σ must be corrected by the factor

$$\exp(-U/kT) \quad (8)$$

But in the case where the change of this factor is not so large in the frequent range of σ , we can take only the first term of the expansion at the neighbourhood of $\sigma = \sigma_0$. Then we have

$$\langle \sigma^2 \rangle = b^2 a^2 n / 18 + \sqrt{3} v u n^{1.5} / 4 \pi b a k T \quad (9)$$

$$\langle \sigma^3 \rangle = 4 b^3 a^3 n^{1.5} / 81 \sqrt{3} + (15\pi - 32) v u n^2 / 64 \pi^{2.5} k T \quad (10)$$

The equation (9) giving the mean square of radius of gyration has the correction term proportional to $n^{1.5}$. This term is positive, when u is positive or in other words the solvation makes the energy low and the force between the parts of chain is repulsive. In the contrary this term is negative, when u is negative or in other words the solvation does not lower the energy and force is attractive. The behaviour of the second term of the equation (10) is quite similar.

It must be noticed that the ratio of the second term to the first term is proportional to $n^{0.5}$ and becomes larger with the increasing value of n . For it has been expected that the ratio of corrections of this kind tends to zero in the limiting case $n \rightarrow \infty$.

5. Specific viscosity . . . approximation.

If specific viscosity η_{sp} is given by Debye's formula

$$\eta_{sp}/c \propto \langle \sigma^2 \rangle \quad (11)$$

where c is the weight concentration of the solution, eq. (9) leads to

$$\eta_{sp}/c = C_1 n + C_2 n^{1.5} \quad (12)$$

in which C_1 and C_2 are constants and their ratio must be

$$C_2/C_1 = 9\sqrt{3}vu/2\pi^2b^3a^3kT = 0.788vu/b^3a^3kT \quad (12a)$$

If η_{sp} is given by Einstein's formula

$$\eta_{sp}/c \propto \langle \sigma^3 \rangle / n \quad (13)$$

where $\langle \sigma^3 \rangle$ is assumed to be proportional to the effective volume, then eq. (10) leads to

$$\eta_{sp}/c = C_1 n^{1.5} + C_2 n^2 \quad (14)$$

in which

$$C_2/C_1 = 81\sqrt{3}(15\pi-32)vu/16^2\pi^2b^3a^3kT = 0.838vu/b^3a^3kT \quad (14a)$$

The value given by (12a) and (14a) contains no arbitrary constant. Now let us try a crude numerical estimation. In paraffine molecule the flexibility constant b^2 is about 6 according to the preceding paper. The contact energy u is assumed to be of the magnitude of the thermal energy kT . And the contact range v is probably about a^3 , the volume of the cube with edges of the length of a C-C bond. Then C_2/C_1 in (12a) and (14a) is about 0.005, and the ratio of the second term to the first term in (12) or (14) becomes about $0.05n^{0.5}$. The correction amounts 50% even in the case where n is only 100. This result shows a cause of the failure of the formula of Staudinger's type

$$\eta_{sp}/c = \text{const. } n^\alpha, \alpha = 0.5 \sim 1 \quad (15)$$

in applying over the wide range of n (Fig. 5).

This numerical value however seems to be somewhat contradictory to the assumption adopted in the approximation of eq. (8), that the correction is small. We must calculate more accurately.

6. Accurate formulae for repulsion.

Rewriting the factor (8) as

$$U/kT = \beta\sigma^{-3} \quad (16)$$

we calculate the numerical integrations

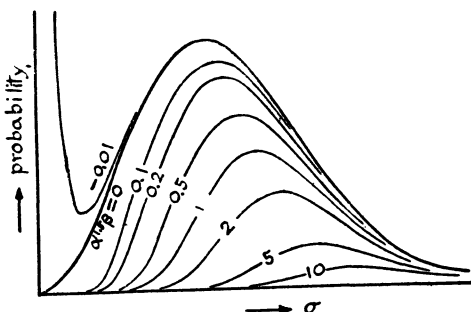


Fig. 3. The effect of intramolecular contacts on the distribution probability of σ .

$$\begin{aligned}\langle \sigma^2 \rangle &= \int \sigma^4 \exp(-\alpha \sigma^2) \exp(-\beta \sigma^{-3}) d\sigma / \int \sigma^2 \exp(-\alpha \sigma^2) \exp(-\beta \sigma^{-3}) d\sigma \\ &= 1.5 \alpha^{-1} (1 + f_2)\end{aligned}$$

$$\begin{aligned}\langle \sigma^3 \rangle &= \int \sigma^5 \exp(-\alpha \sigma^2) \exp(-\beta \sigma^{-3}) d\sigma / \int \sigma^2 \exp(-\alpha \sigma^2) \exp(-\beta \sigma^{-3}) d\sigma \\ &= 4\pi^{-0.5} \alpha^{-1.5} (1 + f_3)\end{aligned}$$

and obtain the numerical values of f_2 and f_3 as the functions of $\alpha^{1.5}\beta$. (Fig. 4). They are proportional to $\alpha^{1.5}\beta$ when they are small, and proportional to the 0.4th and the 0.6th power of it respectively when they are large. Eqs. (4) and (16) give

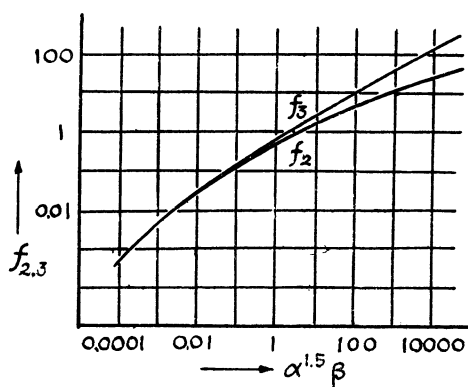


Fig. 4. The correction ratio f_2, f_3 .

$$\begin{aligned}\alpha^{1.5}\beta &= (27/b^2 a^2 n)^{1.5} v n^2 / 16^{1.5} kT \\ &= 1.575 v n^{0.5} / b^3 a^3 kT\end{aligned}$$

Therefore f_2 and f_3 are proportional to $n^{0.5}$ for small n , and proportional to $n^{0.2}$ and $n^{0.3}$ respectively for large n (Fig. 4).

If the specific viscosity is given by Einstein's formula (13), we have

$$\begin{aligned}\eta_{sp}/c &= \text{const.} n^{0.5}(1+f_3) \\ &\cong C_1 n^{0.5} + C_2 n^{0.8}, \text{ for large } n\end{aligned}\quad (17)$$

where

$$C_2/C_1 = 2.08(vu/b^3 a^3 kT)^{0.6}$$

The numerical ratio of the correction term to the first term is about 70% for $n = 100$, and about 300% for $n = 10000$ (Fig. 5).

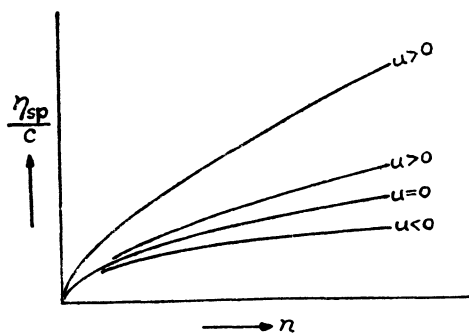


Fig. 5. The relation of viscosity to the molecular weight, and contact energy u .

We can obtain another formula from Debye's (11):

$$\begin{aligned}\eta_{sp}/c &= \text{const.} n(1+f_2) \\ &\cong C_1 n + C_2 n^{1.2}, \text{ for large } n\end{aligned}\quad (18)$$

7. Self-coagulation by attraction.

If the interaction is attractive and u is negative, β in eq. (16) becomes negative and the factor $\exp(-\beta\sigma^{-3})$ ascends so steeply when σ tends to 0 that the distribution of σ is concentrated at $\sigma = 0$. (Fig. 3). The averages of σ are 0. This means the self-coagulation of a chain molecule owing to its own attractive interaction. So far as the interaction is repulsive the molecule has the configuration of the form of the traces of a Brownian particle or its modification, but when the interaction is attractive the configuration becomes as compact as possible however small be the attraction.

Of course σ can not be just 0, because the smallest σ is that of the closest packed sphere of the molecule. But it may be regarded as 0 for large n in comparison with the loose extended form of the repulsive case. If we can alter the interaction gradually from repulsion to attraction by the change of the temperature or the change of the composition of the solvent, we must find the sudden contraction of the size

of the molecule at the moment when the solvation energy turns from positive to negative. It is similar to a phase change.

An example of the self-coagulation into the spherical form in bad solvent is given by the photograph of a polymer molecule by the electron microscope method, where the solvent is the worst one, the air or the vacuum.

If the number of elements n is not so large, the contraction may be gradual. For in this case the size of the closest packed sphere is not negligible so that the concentration of the distribution at $\sigma = 0$ is incomplete. The incompleteness is not discussed here. But it is easily proved that we can obtain the approximation formulae (9), (10), (12) and (14) by cutting off the range of the false concentration into the spherical form of the distribution.

Summary.

In order to express the apparent size of a flexible long chain molecule the radius of gyration σ around the centre of mass is an appropriate quantity, and its mean square $\langle\sigma^2\rangle$ has been considered to be proportional to the number of elements of the chain n .

We estimate the effect of the intramolecular interaction and find new equations

$$\langle\sigma^2\rangle = \text{const.}n + \text{const.}n^{1.5}$$

$$\langle\sigma^3\rangle = \text{const.}n^{1.5} + \text{const.}n^2$$

Specific viscosity η_{sp} divided per weight concentration c must be

$$\eta_{\text{sp}}/c = \text{const.}n + \text{const.}n^{1.5}$$

or

$$\eta_{\text{sp}}/c = \text{const.}n^{0.5} + \text{const.}n$$

In these equations the second term can never be neglected for large n . It amounts to one half of the first term even in the case of normal paraffine with only 100 carbon atoms.

For large n the accurate formula

$$\eta_{\text{sp}}/c = \text{const.}n^{0.5} + \text{const.}n^{0.8}$$

is obtained in the case of repulsive interaction, but in respect to the molecule of large molecular weight with attractive interaction the self-coagulation into the very small size is concluded.

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The Quantum-Mechanical Treatment of Viscosity Coefficient of Helium by Use of a Rigid Sphere Model with Attractive Force.

By Kozo HIROTA.

(Received Sept. 1, 1948.)

1. Introduction.

In the former reports^{(1), (2)}, it was studied if the quantum-mechanical effect can fill up the gap between theoretical and experimental temperature dependency of the viscosity coefficient, and it was concluded definitely that the effect is short of explaining the gap in case of helium, so far as the rigid elastic sphere model is concerned. Therefore, the next step to be taken will be the introduction of molecular interaction in the calculation, as Massay and Buckingham⁽³⁾ already did by use of Slater's potential. However, it was obliged to conclude that the concordance attained by them was limited in some narrow temperature-range, because the evaluation on higher temperatures was hindered by the cumbersome numerical integration. The final aim of the theory, therefore, has not been attained yet.

It is the object of the present paper to introduce a relatively less complicated model in the calculation, with the view to investigate the contribution of the molecular attraction on the collision phenomena. The well-known "Sutherland" model was adopted, assuming the potential form of inverse cube-law-force was the attractive potential to be utilized, i. e.,

$$V(r) = \infty, \text{ if } r < r_0 \text{ and } \beta/r^2, \text{ if } r > r_0 \quad (1)$$

where β denotes a constant and r_0 is the least distance of the molecular encounter.

The above attraction potential was adopted mainly for convenience's sake of the calculation, even though it is slightly improper as compared with the potential form of the sixth order, now acknowledged generally.

In the present report, the calculation was carried out on helium, keeping other assumptions as similarly as in the former report.⁽²⁾

II. Theoretical Formula.

(1) K. Hirota, A. Takahashi, and T. Yoshitomi, this Bulletin, **20** (1947), 1.

(2) K. Hirota, this Bulletin **19** (1944), 102.

(3) H.S. Massay and R. A. Buckingham, *Proc. Roy. Soc., A*, **168** (1938), 304.

The aim of this paper can be reduced to a mathematical problem of evaluating the term (R) which is dependent on molecular interaction in Chapman-Enskog's formula⁽⁴⁾ of the viscosity by use of such a model as (1):

$$\eta = \frac{10\kappa^2 T^3}{\mu} \left(\frac{4\pi\kappa T}{\mu} \right)^{\frac{3}{2}} \frac{1 + \epsilon_1 + \epsilon_2 + \dots}{\pi R} \quad (2)$$

where

$$R = \frac{1}{2} \int_0^\infty Q_\eta v^7 e^{-\frac{uv^2}{\kappa T}} dv \quad (3)$$

ϵ_ν : the ν -th order approximation term; Q_η : viscosity "Cross-section"; κ : Boltzmann's constant; μ and v : reduced mass and velocity of the colliding molecules, respectively; T : absolute temperature.

In the treatment, the first order approximation term (ϵ_1) was only calculated, while the higher order approximation terms (ϵ_2 , ϵ_3 , etc.) were neglected, according to the conclusion in the previous paper⁽¹⁾ that they are small irrespective to the model adopted.

The viscosity cross-section is given by⁽⁵⁾

$$Q_\eta = \frac{2\pi}{k} \sum_n \{1 + \tilde{\epsilon}^n\} \left\{ \sin^2 \delta_n \frac{4n^3 - 6n^2 - 2n + 2}{(2n+1)(2n+3)} - \cos(\delta_n - \delta_{n-2}) \sin \delta_n \sin \delta_{n-2} \frac{2(n+1)(n+2)}{2n+3} \right\} \quad (4)$$

where $k = \frac{2\pi\mu v}{h}$ and $\tilde{\epsilon}$ equals to 0, 1, -1 according as the statistics is Boltzmann's, Bose-Einstein's or Fermi-Dirac's, respectively, and -1 was utilized throughout in this paper, because collisions of similar molecules were only dealt with. Summation was carried out with respect to all the scattered de Broglie's waves, and δ_n 's are their phases which are to be determined from the solution of the wave equation with the boundary condition (1), i.e., the wave amplitude is zero at the molecular distance of r_0 .

As the field is symmetrical to the centre of the scattering molecules, the problem is reduced to the solution of the radial part of the wave function u :

$$\frac{d^2 u}{dr^2} + \left\{ k^2 + \frac{n(n+1)}{r^2} - \frac{8\pi^2\mu}{h^2} V(r) \right\} u = 0 \quad (5)$$

(4) Chapman and Cowling, "Mathematical Theory of Non-Uniform Gases", Cambridge (1939).

(5) Cf. Chapman and Cowling, *ibid.*, Chapt. 17.

where r is the radial distance from the molecular centre of the colliding molecules.

Under the assumptions of (1),

$$\frac{d^2u}{dr^2} + \left\{ k^2 + \frac{n(n+1)-\gamma}{r^2} \right\} u = 0 \quad (5')$$

where $\gamma = 8\pi\mu\beta/h^2$ at $r > r_0$ and 0 at $r < r_0$, the general solution is given by

$$U = \sqrt{r} \{ A J_{\nu_+}(kr) + B J_{\nu_-}(kr_0) \} \quad (6)$$

where ν_+ and ν_- denote $\nu_{\pm} = \frac{1}{2}(-1 \pm \sqrt{(2n+1)^2 + 8})$, respectively.

The derivation of this formula is given by Mott and Massay.⁽⁶⁾

Taking the boundary condition $u = 0$ at r_0 into consideration, we obtain

$$\delta_n = \text{arctg} (-1)^n \{ J_{\nu_+}(kr_0) / J_{\nu_-}(kr_0) \} \quad (7)$$

where

$$v = (kh') / (2\pi\mu) \quad (8)$$

III. Calculation and Results.

The numerical constants adopted in the calculation are as follows. The value of r_0 was assumed as 2.0 Å, because it was the best one in case of rigid elastic sphere models. The value of β was assumed as 8.9×10^{-32} c. g. s. and 1.12×10^{-32} for case A and B, respectively. They correspond to the assumption that the least energy at the distance of the molecular contact is, respectively, 800 and 1000 cal. Probably the least energy of attraction in the actual potential curve will exist within the two values. In other words, the attractive potential of liquid helium is estimated as such from the thermodynamic properties.

The procedure of calculation was perfectly similar to the case of rigid elastic sphere except the cumbersome evaluation of the Bessel function of non-integral orders. This most difficult procedure of the calculation was, however, simplified by the extrapolation of the values of Bessel functions $J_m(z)$ calculated by us.⁽⁷⁾

Thus it became possible to calculate the ratio of the quantal cross-section to that of the classical value (Q_n/Q_{n0}) in each two cases. The

(6) "Atomic Collisions", Oxford (1933), Chap. 1.

(7) Generally ν 's in (6) become irrational numbers, so they are evaluated only when m equals to 0, 0.1, ± 0.1 , ± 0.2 , ± 0.3 , ..., ± 4.9 , 5.0. It was found that values larger than $m = 5$ were unnecessary in the present object.

results are shown by Table 1 together with that by use of a rigid elastic sphere model, as the function of kr_0 . As is known the attractive potential made the effective collisional area larger, and the ratio is fairly near to that of a rigid elastic sphere model in case of small attractive potential (case B). It is also found that the larger the kr_0 , the less is the effect, and in case of large attractive potential (case A), it is needless to calculate the values higher than $kr_0 > 10$, because they are practically equal to that of a rigid elastic sphere model.

By use of the values of case A, η was calculated according to (2), those of similar collisions being used. It was found that the effect of the attractive potential became marked at lower temperatures, and at 88.8°K the effect does not bring any change of figures (101.8×10^{-6}). However, it is clearly shown that introduction of such attractive potential contributes, to some extent, to fill up the gap hitherto found in case of rigid elastic sphere models. (cf. the last column of Table 2.)

Table 1. Effective "Cross-section" (Q_η/Q_{r_0}).

kr_0	Similar Collision			Dissimilar Collision		
	Rigid E. Sp. Model	Sutherland Model		Rigid E. Sp. Model	Sutherland Model	
		Case A.	Case B.		Case A.	Case B.
0.	8.000			4.000		
0.5	7.342			3.709		
1	5.535	6.673	5.63	3.108	3.64	3.18
1.5	3.585	3.727	—	2.556	2.500	—
2	2.287	2.163	2.271	2.168	2.217	2.17
2.5	1.866	1.895	—	1.653	1.973	—
3	1.757	1.960	1.795	1.780	2.075	1.809
4	1.596	1.638	1.599	1.570	1.642	1.598
5	1.466	1.448	1.462	1.468	1.498	1.464
7	1.327	1.332	—	1.329	1.345	—
10	1.234			1.229		
15	1.150			1.149		
20	1.113			1.110		
25	1.088			1.097		
30	1.070			1.070		
40	1.049			—		
50	1.039			—		

N. B. (Case A. the least energy of attractive force 800 cal.
Case B. 1000 cal.

On the other hand, it was found that larger values of β can make the η -values at 15°K smaller as much as we desire, though they cannot do so at 89°K at the same time. Such tendency can be amended, if

Table 2. Calculated and Experimental Values of Viscosity Coefficient of Helium.

T°K	Viscosity Obser.	Classical	Viscosity R. E. Sp.	calculated Model	Sutherland M.
		Value	$r_0=2.0$ A	$r_0=2.1$ A	$r_0=2.0$ A
1090	471.3	368	415.8	378.8	(415.8)
879	408.7	347	370.7	—	(370.7)
680	343.6	313	323.2	294.6	(323.2)
473	267.2	255	264.8	—	(264.8)
273.1	187.0	193	194.9	198.9	(194.9)
170.5	139.2	154	148.9	—	(148.9)
88.8	91.8	110	101.5	93.4	(101.8)
15.0	29.5	46	32.5	30.5	31.9

N. B. Values in parenthesis are the same as in the 4-th column.

we adopt a slower inclination of the repulsive potential. Thus we can get generally to a fairly good concordance of the theory and experiment, so far as monoatomic molecule is concerned.

Summary.

By use of a rigid sphere molecule model with attractive force of inverse cube law the viscosity coefficient of helium was calculated quantum-mechanically. It was found that the gap hitherto known between theory and experiment has become smaller at low temperatures than in case of no attractive force.

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Studies on Foams. II.

The Foam Formation and the Volume Contraction of Liquid Mixtures.

By Masayuki. NAKAGAKI.

(Received Sept. 6, 1948.)

It has been reported, in the preceding paper,⁽¹⁾ that there are the maxima of the foam formation in three regions in the ternary system, ethyl alcohol-glycerol-water, that is the region of small concentration of ethyl alcohol, where the surface tension of the system decreases steeply, the region of large concentration of glycerol, where the viscosity of the system becomes very large, and the region of about 45 per cent of ethyl alcohol. The third maximum is thought to be closely connected with the volume contraction on admixture of the constituent liquids. This may be confirmed by the experiments, on the mixture of methyl alcohol, ethyl alcohol and water which is described in the following lines.

The experimental method is similar to that described in the preceding report. Foaminess and foam duration have been tested by shaking the liquid for 30 seconds in a test tube, measuring the height of foam zone immediately after the end of shaking (A_0 cm.), and the time required to the collapse of foam zone (t sec.). Viscosity η was measured with Ostwald's viscosimeter, and surface tension γ was measured with Traube's stalagmometer. Molar volume contraction ΔV on admixture of liquids (cc./mol.) was calculated from the density data obtained with an Ostwald's pycnometer.

The results obtained are shown in Fig. 1 and Fig. 2. The composition dependence of foaminess A_0 (Fig. 1), and foam duration t (Fig. 2), are entirely parallel with each other, having three maxima, A_1 , A_2 , and B_1 . The maximum B_1 is, perhaps, related with the steep decrease of the surface tension, shown in Fig. 3. The maxima A_1 and A_2 , on the other hand, have no relation either to surface tension or to viscosity (Fig 4). These

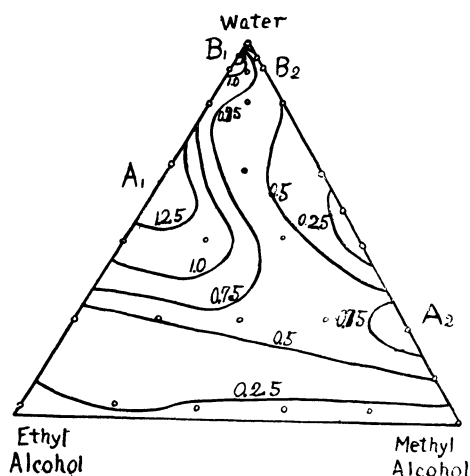


Fig. 1. Foaminess.
 A_0 (cm.).

(1) The first paper, this Bulletin, 21 (1948), 30.

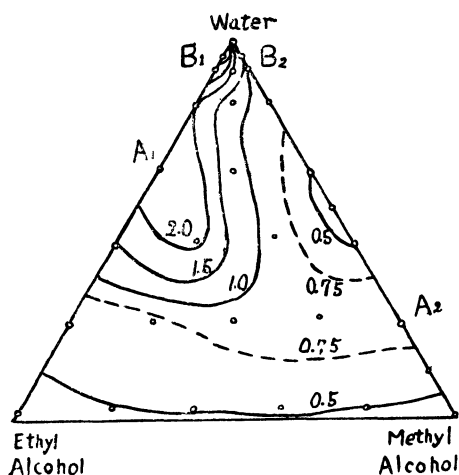


Fig. 2. Foam Duration.
 t (sec.).

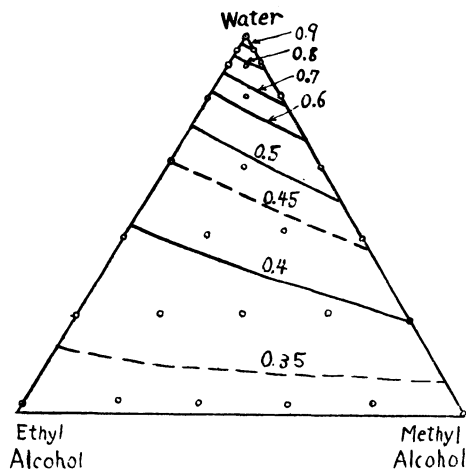


Fig. 3. Surface Tension.
 r/r_w .

maxima seem to have some relation with the volume contraction (Fig. 5). Besides the ternary system, ethyl alcohol-methyl alcohol-water, the following five binary systems have been studied: *n*-propyl alcohol-ethyl ether, methyl alcohol-ethyl ether, ethyl acetate-ethyl ether, *n*-propyl alcohol-methyl alcohol and *n*-propyl alcohol-ethyl acetate. In most of these systems it was confirmed that the molar volume contraction is closely related to the foam formation. The system *n*-propyl alcohol-ethyl ether and methyl alcohol-ethyl ether have relatively large volume contraction and foam formation. The other systems have small volume contraction or dilatation and little tendency of foam formation.

The binary mixture of the liquid A and B may, generally, be classified into the following three types:

(a). If the molecular interaction between molecules A-B is nearly equal to the average of A-A and B-B, heat of mixing and volume contraction on admixture are both small, and they form the ideal solution. The systems *n*-

propyl alcohol-methyl alcohol, and methyl alcohol-ethyl alcohol belong to this type, and they do not foam.

(b). If the interaction A-B is smaller than the average of A-A and B-B, heat absorption and volume dilatation may be observed. The system *n*-propyl alcohol-ethyl acetate belongs to this, and this system does not foam.

(c). If the interaction A-B is larger than the average of A-A and B-B, heat evolution and volume contraction on admixture are observed. In this case, according to McLeod,⁽²⁾ viscosity-composition curve has a maximum point. Examples are the systems, ethyl alcohol-water and methyl

(2) McLeod, *Trans. Faraday Soc.*, **19** (1923), 17.

alcohol-water, the foam formation of which becomes maximum at the composition of about 1 : 1.

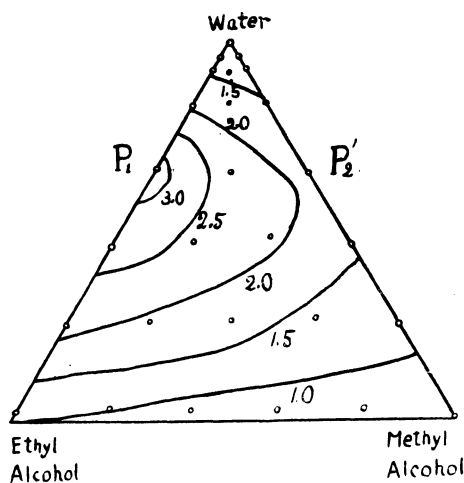


Fig. 4. Viscosity.
 η/η_w .

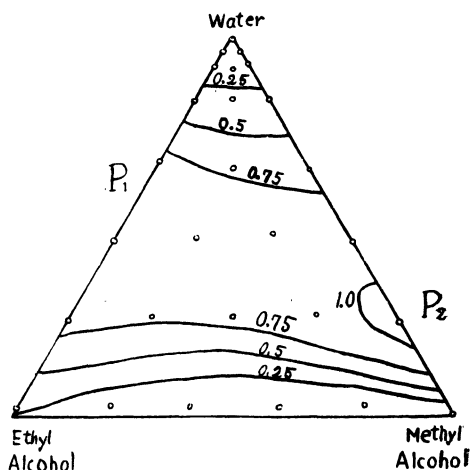


Fig. 5. Volume Contraction.
 ΔV (c.c./mol.).

Two mechanisms are proposed on the volume contraction. One is the increase of the average molecular interaction and the decrease of the average molecular distance, which may be corresponding to the case (c) described above. The other is the micelle formation of one of the constituent liquids. By the micelle formation the molecular motion will be restricted in some extent and the free volume of molecules may decrease. The idea that such a micelle is formed not only in aqueous solutions but also in the mixtures of organic liquids was already proposed by S. R. Palit and J. W. McBain.⁽³⁾ The properties based on the simultaneous presence of the polar and nonpolar portions, or "amphipathic properties", of the solute molecule was considered by G. S. Hartley⁽⁴⁾ as an essential factor of micelle formation.

Now a series of solvents, water, acetone, ethyl acetate, and ether will be considered. The hydrophile properties of them become weaker and the organic characters become stronger in this order. They mix with alcohol at any proportion, and according to H. Hirobe,⁽⁵⁾ the volume change on admixture is large contraction for water, small contraction for acetone, dilatation for ethyl acetate, and, again, contraction for ether. Micelle may, probably, be formed in water, acetone and ether, but not in ethyl acetate. Therefore, it is supposed that water and acetone have

(3) S. R. Palit and J. W. McBain, *Ind. Eng. Chem.*, **38** (1946), 741.

(4) G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts", London (1936), Chap. 7.

(5) H. Hirobe, *J. Faculty of Sci. Imp. Univ. Tokyo*, Sec. 1, **1**, Part 4 (1926), 155.

a stronger affinity for hydroxyl group of alcohol than for alkyl group, but ethyl acetate has nearly equal affinity for both groups, and ether has a stronger affinity for alkyl group than for hydroxyl group. Then, according to the experiments described above, the liquid mixtures, in which micelle are formed, have foam forming properties.

The foam formation is one of the characteristic properties of the solution. The pure liquid does not foam, however small the surface tension is. This fact was assured by C. W. Foulk and J. N. Miller,⁽⁶⁾ T. Nakagawa and J. Sameshima,⁽⁷⁾ and others. It is, therefore, supposed that the existence of the Gibbs' adsorption layer at the surface is important for the foam formation. As stated by C. R. Caryl,⁽⁸⁾ E. G. King,⁽⁹⁾ and G. D. Miles and J. Ross,⁽¹⁰⁾ the surface activity and some other surface chemical properties are closely related to "diphile nature",⁽¹¹⁾ or "amphipathic nature", of solute molecule, and this is also the cause of micelle formation. It is, therefore, reasonable that the foam formation and micelle formation accompany with each other.

Summary.

The foam formations were tested on the ternary system, methyl alcohol-ethyl alcohol-water, and five binary mixtures. It was found that the volume contraction is closely connected with the foaming properties. This was interpreted in relation to the micelle formation of mixtures.

The author wishes to express his hearty thanks to Professor J. Sameshima for his kind guidance and encouragement.

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(6) C. W. Foulk, *Ind. Eng. Chem.*, **21** (1929), 815; **33** (1941), 1086; C. W. Foulk and J. N. Miller, *ibid.*, **23** (1931), 1283.

(7) T. Nakagawa and J. Sameshima, *J. Chem. Soc. Japan*, **64** (1943), 360.

(8) C. R. Caryl, *Ind. Eng. Chem.*, **33** (1941), 731.

(9) E. G. King, *J. Phys. Chem.*, **48** (1944), 141.

(10) G. D. Miles and J. Ross, *J. Phys. Chem.*, **48** (1944), 280.

(11) Wo. Ostwald, *Kolloid-Z.*, **58** (1932), 179; **60** (1932), 324.

General Expressions of the Chemical Compositions of the Fine Micac and Chlorites.

Toshio SUDÔ.

(Received July 15, 1948.)

1. General expression

The chemical compositions of so-called fine micac, such as sericite⁽¹⁾, hydro-mica⁽²⁾, hydro-muscovite⁽³⁾, secondary mica⁽⁴⁾, glimmerton⁽⁵⁾, potassium bearing clay minerals⁽⁶⁾, illite⁽⁷⁾, glauconite and celadonite⁽⁸⁾, have been discussed by several authors, but these discussions had no basis on the standpoint of crystal structures. On the other hand, the crystal structure of mica, such as muscovite, was determined and the general formula of mica has been shown to be as follows⁽⁹⁾:



(Where X : K, Na, Ca ; Y : Al, Fe^{III}, Fe^{II}, Mg, Mn, Cr, Ti, Li, V, etc. ;
Z : Si, Al)

This formula has not been adapted to the chemical compositions of the fine micac above enumerated. The writer re-examined the chemical compositions of the fine micac by the general structural formula of mica, that is, the writer summarized the accurate and already reported chemical compositions of fine micac (Table 1. 2), and from these, the writer calculated X, Y, and Z of the formula above described, and values of X, Y, and Z thus calculated were plotted on the triangular diagram as shown in Fig. 1, (a), and (b).

(1) E. V. Shannon, *U. S. Natl. Museum Bull.*, **131** (1926), 367; J. Jakob, C. Friedlaender and E. Brandenberger, *Schweiz. Mineralog. u. Petrog. Mitt.*, **13** (1933), 74; P. Niggli, *ibid.* **13** (1933), 84; J. Jakob, *Z. Krist.*, **69** (1929), 511; B. Kotô, *J. Coll. Sci. Imp. Univ. Tokyo*, **2** (1888), 89.

(2) W. S. Bradley, *Econ. Geol.*, **15** (1920), 236; R. E. Somer, *J. Wash. Acad. Sci.*, **9** (1916), 113; A. Brammall, *Mineralog. Mag.*, **24** (1937), 507.

(3) G. Nagelschmidt, *Z. Krist.*, **97** (1937), 514.

(4) G. M. Schwartz and R. J. Leonard, *Am. J. Sci.*, **11** (1926), 262.

(5) K. Fndell, U. Hofmann, and E. Maegdefrau, *Zement*, **24** (1935), 625.

(6) C. S. Ross and P. E. Kerr, *J. Sed. Petr.*, **1** (1913), 59.

(7) R. E. Grim, R. H. Bray and W. F. Bradley, *Am. Mineral.*, **22** (1937), 813.

(8) Recently it has been shown that the types of glauconite and celadonite are similar in their X-ray powder patterns to those of micac. J. W. Gruner, *Am. Mineral.*, **20** (1935), 699; E. Maegdefrau and U. Hofmann, *Z. Krist.*, **97** (1937), 514.

(9) Ch. Mauguin, *Comp. rend. Acad. Sci. Paris*, **185** (1927), 288; **186** (1928), 879, 1131; L. Pauling, *Proc. Nat. Acad. Sci. U. S. A.*, **16** (1930), 123; W. W. Jackson and J. West, *Z. Krist.*, **76** (1931), 211; W. L. Bragg, "Atomic Structure of Minerals," 1937, 213.

Table I. (Sericite).

	(1)	(2)***	(3)***	(4)	(5)	(6)
SiO ₂	46.58	50.39	50.05	45.64	47.14	53.01
TiO ₂		0.42	0.14	1.81		
Al ₂ O ₃	37.46	29.74	30.11	33.59	37.13	34.70
Fe ₂ O ₃	0.80	1.61	1.47	1.96	0.64	tr.
Cr ₂ O ₃						
FeO		0.38	0.43	0.38		
MnO		0.01	0.01	0.10		
CaO	tr.	0.00	0.00	0.00	0.71	0.27
MgO	1.16	2.40	2.49	2.33	0.17	0.50
Na ₂ O	0.64	2.62	1.97	1.59	0.65	1.01
K ₂ O	6.38	9.97	9.80	8.81	9.98	6.05
H ₂ O(+)	6.06	2.55	3.58	3.89⊗	4.23* }	4.67**
H ₂ O(-)	0.30			0.00⊕		
F						
Total	99.38*	100.09	100.05	100.10	100.70	100.21

Note: * Ig. loss. ** H₂O. *** analyses on material dried at 110°C.
 ⊗ > 110°C. ⊕ < 110°C.

(1) The Carrol-Driscoll Mine, Idaho. E. V. Shannon, *U. S. Natl. Museum, Bull.*, **131** (1926), 367.

(2) Werkkanals des Rheinkraftwerks, Albdruk-Dogern. Occurs in gneiss. Coarse grains accumulated by water dressing. J. Jakob, C. Friedlaender and E. Brandenberger: *Schweiz. Mineralog. u. Petrog. Mitt.*, **13** (1933), 74; P. Niggli: *Schweiz. Mineralog. u. Petrog. Mitt.*, **13** (1933), 84.

(3) As (2), fine grains.

(4) Campra bei Olivone, Kanton Tessin. Fine scales in sericite biotite schist, forming nests partly. J. Jakob: *Z. Krist.*, **69** (1929), 511.

(5) The Hitachi Mine, Ibaragi Prefecture. K. Seto: *J. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, **1**, (1929), 124.

(6) Ōtakisan in Tokushima Prefecture. B. Kotô: *J. Coll. Sci. Imp. Univ. Tōkyō*, **2** (1888), 89.

From these figures the following general facts are recognized:

(1) The plotting points of the colourless fine micas such as sericite, hydro-mica, secondary mica, illite, etc., and the plotting points of the chemical compositions of glauconite and celadonite fall in the same area. (Fig. 1, (a), (b)).

(2) The fine micas have, as a rule, less X(K, Na, Ca) and more Y(Al, Fe''', Fe'', Mg, etc.) than muscovite (M), and such fluctuation is largest in illite. (Fig. 1, (a)).

(3) From Fig. 1 (b) the differences in the chemical compositions of glauconite and celadonite are not clearly shown.

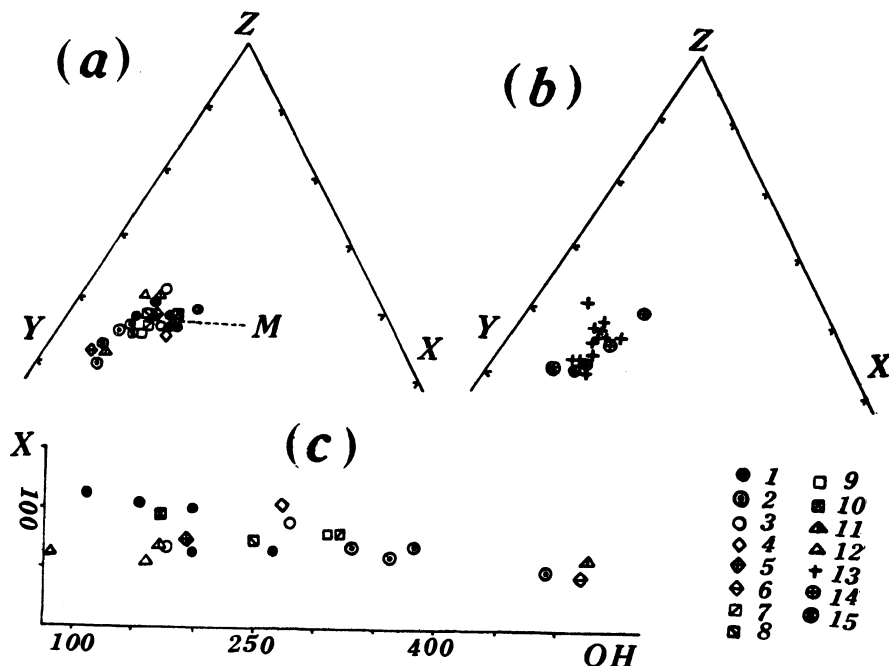


Fig. 1. 1, Sericite; 2, Illite; 3, Phengite; 4, Alurgite; 5, White mariposite; 6, Hydro-mica; 7, Hydro-muscovite; 8, Secondary muscovite; 9, Damourite; 10, Gilbertite; 11, Micas altered from spodumene; 12, Micas reported by E. Maegdefrau and U. Hofmann; 13, Glauconite; 14, Celadonite; 15, "Grünerde" (by K. Hummel); *M*: Mean value of the chemical compositions of muscovite (by W. Kunitz, *Neues Jahrb. Mineral. Geol.*, Beilage-Band, A, 50 (1924), 365.)

2. Relation between (OH) and (K, Na, Ca) of the fine micas.

Next the writer compared the content of (OH)⁽¹⁰⁾ and that of X(K, Na, Ca) as shown in Fig. (1), (c). It is shown, from Fig. 1, (c), that the content of (OH) is roughly inversely proportional to the content of X(K, Na, Ca). The writer also compared the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the content of X(K, Na, Ca), but no fixed ratio has been found between these values.

In the chemical compositions of glauconite and celadonite, we could not recognize the fixed ratio between the values of (OH) and X(K, Na, Ca), or (OH) and the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$.

3. $\text{R}_2\text{O}_3/\text{RO}$ in glauconite and celadonite.

In Fig. 1, (a) and (b), the differences between the chemical compositions

(10) It is a very difficult problem to solve the state of the water in the crystal structures of such fine micas. In the chemical analyses reported in literatures, the water contents are described in various forms, such as $\text{H}_2\text{O}(+)$ and $\text{H}_2\text{O}(-)$ or only as H_2O or as ignition loss. Generally the content of $\text{H}_2\text{O}(-)$ is small, and the writer used the value of $\text{H}_2\text{O}(+)$ when the content of water is described separately as $\text{H}_2\text{O}(+)$ and $\text{H}_2\text{O}(-)$, and in other cases, he used the total content of water or ignition loss.

Table 2.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO ₂	52.58	58.90	53.22	56.79	47.29	53.47	40.79	46.54	46.54
TiO ₂				25.29			1.28	0.17	
Al ₂ O ₃	23.56	25.28	21.19		31.31	32.36	29.98	36.37	30.39
Fe ₂ O ₃		2.30	1.22	1.59	1.19	0.79	8.07	0.72	4.42
FeO	5.76				0.37	0.42	2.48	0.36	2.98
Mn ₂ O ₃			0.87						
MnO			0.18			0.72			
CaO	0.65	0.65		0.07	0.69	0.17	0.45	0.22	0.35
MgO	2.43	1.49	6.02	3.29	2.38		2.71	0.50	0.94
Na ₂ O		1.37	0.34	0.17	0.88	0.44	0.38	0.46	1.44
K ₂ O	9.52	5.73	11.20	8.92	4.07	7.68	3.47	8.06	5.57
H ₂ O(+)	5.94* }	4.14* }	5.75* }	4.72* }	9.92** }	4.07* }	9.34 }	6.83* }	5.31**
H ₂ O(-)									
F								0.02	0.58
Total	100.44	99.86	99.99	100.84	(100.26)	(100.16)	(100.15)	100.25	98.52

Note: *H₂O; **Ig. loss; †Ig. loss on material dried at 110°C; ††Ig. loss on material

(1) Phengite (Wildschapbachtal). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 428.

(2) Phengite (Witticher Tal). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 428.

(3) Alurgite. (A manganese mine at St. Marcel, Piemont, Italy). S. L. Penfield, *Z. Krist.*, **25** (1896), 277.

(4) White mariposite (The Josephine Mine, Bear Valley, California). W. L. Hillebrand, *U. S. Geol. Survey Bull.*, **167** (1900), 74. Cr₂O₃: none.

(5) A. micaceous mineral altered from spodumene (The Etta mine, South Dakota), G. M. Schwarz and R. J. Leonard, *Am. J. Sci.*, **11** (1926), 262. Li₂O: 0.28.

(6) A micaceous mineral altered from spodumene (Branchville, Connecticut). G. J. Brush and E. S. Dana, *Z. Krist.*, **5** (1881), 210. Li₂O: 0.04.

(7) Hydro-mica (North Carolina). W. S. Bailey, *Econ. Geol.*, **15** (1920), 236.

(8) Hydro-muscovite. G. Nagelschmidt, *Z. Krist.*, **97** (1937), 514. Li₂O: tr.

(9) Secondary muscovite (Spprechstein). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 426.

Table 2. (Continued).

(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)⊕	(18)⊕
45.72	48.96	50.10	51.22	47.21	52.23	44.01	51.65	50.30
.....		0.50	0.53		0.37	0.64	tr.	tr.
37.17	30.96	25.12	25.91	21.47	25.85	26.81	21.67	32.80
2.18		5.12	4.59	10.73	4.04	11.99	6.20	0.00
.....								
.....	2.24	1.52	1.70				1.24	0.00
.....								
0.05	0.26	0.35	0.16	0.21	0.60	0.11	0.00	0.55
2.00	1.97	3.93	2.84	3.62	2.69	2.43	4.48	1.95
1.44	1.65	0.05	0.17		0.33	0.07	0.31	0.52
6.69	8.47	6.93	6.09	5.78	6.56	4.78	6.08	6.72
6.79* } }	3.83* } }	6.82 † } }	7.49 † } }	10.99 †† } }	7.88 † } }	9.19 † } }	6.44 } }	6.98 } }
....	1.04							
102.04	99.38	100.44	100.70	100.01	100.55	100.03	98.07	99.82

dried in air ; ⊕Chemical ; analysis is of 105°C dried material.

(10) Damourite (Fen Norway). "Doelter's Handbuch der Mineralchemie", II, Part 2 (1917), 422.

(11) Gilbertite (Ehrenfriedersdorf). "Dana's System of Mineralogy", 1914, 618.

(12) Illite (Maquoketa (Ordovician) shale, near Gilead, Calhoun County, Illinois). $H_2O(+)$: 7.18; $H_2O(-)$: 1.90. R. E. Grim, R. H. Bray and W. F. Bradley, *Am. Mineral.*, 22 (1937), 813.

(13) Illite (Pennsylvanian underclay, near Fithian, Vermilion County, Illinois). $H_2O(+)$: 7.14; $H_2O(-)$: 1.45. Ref. as (12).

(14) Illite (IV b horizon of Clarence soil, Ford County, Illinois). $H_2O(+)$: 6.17; $H_2O(-)$: 3.80. Ref. as (12).

(15) Illite (Cretaceous shale, near Theles, Alexander County, Illinois). $H_2O(+)$: 7.88; $H_2O(-)$: 1.13. Ref. as (12).

(16) Illite (Pennsylvanian shale, near Petersburg, Menard County, Illinois). $H_2O(+)$: 8.03; $H_2O(-)$: 2.33. Ref. as (12).

(17) Mica in marl. Small amount of quartz is included in the analysed sample. E. Maegdefrau and U. Hofmann, *Z. Krist.*, 98(1938), 31.

(18) Mica in liparite. Sarospatak, North-east of Mt. Hegyalja. Ref. as (17).

Table 3.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO ₂	51.55	51.38	51.63	51.25	50.75	51.27	53.58	48.66	48.5
TiO ₂	tr.	tr.	tr.	tr.	tr.	tr.	0.07		
Al ₂ O ₃	4.03	4.25	5.01	4.44	6.65	5.45	8.17	8.46	9.0
Fe ₂ O ₃	22.17	23.82	23.09	22.22	21.64	23.14	18.27	18.80	20.0
FeO	3.54	2.91	2.75	3.62	3.41	2.85	2.87	3.98	3.1
MnO	tr.	tr.	tr.	tr.	tr.	tr.	tr.		
MgO	3.86	3.23	3.71	3.53	3.23	3.97	2.95	3.56	3.7
CaO	0.69	0.55	0.35	0.62	0.57	0.49	0.89	0.62	0.4
Na ₂ O	0.55	0.78	0.68	0.94	0.75	0.28	0.94	none	1.5
K ₂ O	7.03	6.82	6.75	6.95	6.92	6.80	5.64	8.31	6.2
P ₂ O ₅	0.03	tr.	0.02	tr.	tr.	tr.	tr.		
CO ₂									
H ₂ O(+)	6.62* }	6.62* }	6.25* }	6.23* }	6.02* }	6.00* }	6.53* }	4.62 }	7.3**
H ₂ O(-)								1.94 }	
Total	100.07	100.36	100.24	99.80	99.94	100.25	99.91	98.95	99.67

Note: *H₂O; **Ig. loss; *** chemical analysis of 105°C dried materials;

(1)-(7) Glauconite from Japan (after T. Yagi) "Glauconite." (in Japanese).

(8) Glauconite. J. W. Gruner, *Am. Mineral.*, **20** (1935), 699; with CO₂, total 99.08.

(9) Glauconite. H. Schneider, *J. Geol.*, **35** (1927), 296.

Table 3. (Continued).

(10)	(11)	(12)***	(13)	(14)	(15)***	(16)	(17)	(18)	(19)
48.12	49.42	49.10	53.61	49.11	55.30	54.30	54.84	54.22	46.65
.....		nb.			nb.	tr.			0.73
9.16	10.23	19.30	9.56	8.03	10.90	5.08	3.52	3.70	17.92
19.10	16.01	7.52	21.46	20.05	6.95	14.77	12.64	12.50	10.09
3.47	3.00	2.87	1.53	3.05	3.54	4.82	4.90	4.75	4.25
.....			tr.			0.09	0.24	0.19	0.07
2.36	3.78	2.71	2.87	3.18	6.56	6.05	6.65	6.98	1.63
0.76	0.31	0.98	1.39	0.87	0.47	0.80	0.89	0.84	1.26
0.22	0.26	0.00	0.42	0.66	0.00	3.82	0.39	0.44	0.69
7.08	7.91	7.50	3.49	6.97	9.38	4.85	7.00	6.90	3.91
.....									0.04
.....									1.66
5.28⊗	} 8.08* }	} 6.07 }	} 5.96* }	} 8.05* }	} 5.21 }	} 5.64* }	} 9.62* }	} 99.9* }	5.07
4.78⊕									5.86
100.33	99.00	96.05	100.34	99.97	98.31	100.22	100.69	100.51	99.83

⊗ > 105°C; ⊕ < 105°C.

- (10) Glauconite. A. F. Hallimond, *Mineralog. Mag.*, **19** (1922), 330.
 (11) As (10); quartz: 0.80%.
 (12) Glauconite. E. Maegdefrau and U. Hofmann, *Z. Krist.*, **98** (1938), 31.
 (13) Glauconite. Mean value of the chemical compositions of glauconite collected by "Challenger". W. H. Twenhofel, "Principles of Sedimentation", 1939, 401.
 (14) Mean value of 12 analyses of glauconite reported by A. F. Hallimond, *Mineralog. Mag.*, **19** (1922), 330.
 (15) Celadonite. W. E. Maegdefrau and U. Hofmann, *Z. Krist.*, **98** (1938), 31.
 (16) Celadonite. A. Lacroix, *Bull. soc. franç. minéral.*, **39** (1916), 93.
 (17) Mean value of celadonite from Scotland. W. H. Twenhofel, "Principles of Sedimentation", 1939, 401.
 (18) Mean value of the chemical analyses of celadonite reported by F. Heddle and L. L. Fermor, *Rec. Geol. Survey, India*, **58** (1926), 141, 330.
 (19) "Grünerde". K. Hummel, *Chem. Erde*, **6** (1931), 468.

of glauconite and celadonite are not clearly shown. The writer showed the difference as follows. From the accurate chemical compositions (Table 3) of glauconite and celadonite⁽¹¹⁾, the writer calculated the values of R_2O_3 ($Al_2O_3 + Fe_2O_3$) and $RO(FeO + MgO)$ as $SiO_2 : 2.00$ and plotted them on Fig. 2. (c). From this figure, it is clearly shown that R_2O_3/RO is less than 1 in celadonite, while, the ratio is larger than 1 in glauconite.

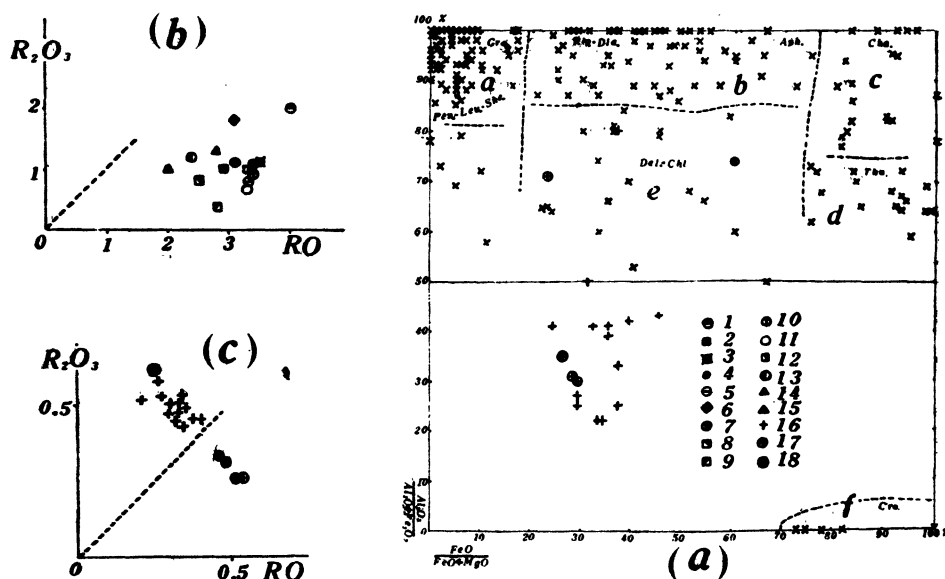


Fig. 2. Diagrammatic expression of the chemical compositions of chlorites, glauconite, celadonite and "Grünerde". x: chlorites.

- (a) Pen.-Leu.-She.-Gro. area: Penninite, Leuchtenbergite, Sheridanite, Grochaulte, etc.
 (b) Rip.-Dia.-Aph. area: Ripidolite, Diabantite, Aphrosiderite, etc.
 (c) Cha. area: Chamosite.
 (d) Thu. area: Thuringite.
 (e) Del. area: Delessite, Chloropite, (Cinochlore, Prochlorite), etc.
 (f) Cro. area: Cronstedite.

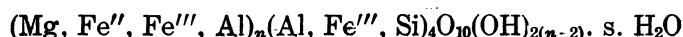
1, Amesite; 2, Aphrosiderite; 3, Bavalite; 4, Chamosite; 5, Clinochlore; 6, Cronstedite; 7, Daphnite; 8, Delessite; 9, Diabantite; 10, Leuchtenbergite; 11, Penninite; 12, Ripidolite; 13, Sheridanite; 14, Strigovite; 15, Thuringite; 16, Glauconite; 17, Celadonite; 18, "Grünerde" (by K. Hummel).

4. General expression of the chemical composition of chlorites.

About the chemical compositions of chlorites, the excellent generali-

(11) T. Yagi, *J. Japan. Assoc. Mineral. Petrol. Econ. Geol.*, **3** (1930), 119 (n Japanese); J. W. Gruner, *Am. Mineral.*, **20** (1935), 699; W. H. Twenhofel, "Principles of Sedimentation," 1939, 401; H. Schneider, *J. Geol.*, **35** (1927), 296; A. F. Hallimond, *Mineralog. Mag.*, **19** (1922), 330; **13** (1298), 68; K. Hummel, *Chem. Erde*, **6** (1931), 468; E. Maedgafrau and U. Hofmann, *Z. Krist.*, **98** (1938), 31; L. L. Fermor, *Rec. Geol. Survey, India*, **58** (1926), 141, 330; A. Lacroix, *Bull. soc. franç. minéral.*, **39** (1916), 93.

zation was reported by J. Orcel⁽¹²⁾. The crystal-structural formula of chlorite has been discussed recently by H. Berman⁽¹³⁾ to be as follows.



Namely the half of (Al, Fe''') replaces a part of Si and the other half of (Al, Fe''') replaces a part of (Mg, Fe'') and it was shown that the various ratios of $\text{RO}/\text{R}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{R}_2\text{O}_3$, and FeO/RO produce many species of chlorite well known. The writer tried a general expression of the chemical compositions of chlorites by above three ratios. First the chemical compositions of chlorite are expressed by the ratio of $\text{R}_2\text{O}_3/\text{RO}$ (where $\text{SiO} : 200$) in Fig. 2, (b). It is clearly shown from Fig. 2, (b) that the ratio of $\text{R}_2\text{O}_3/\text{RO}$ is less than 1 in chlorites. Next the chemical compositions of the main chlorites are plotted in the diagram by the ratio of $\text{Al}_2\text{O}_3/\text{R}_2\text{O}_3$ and the ratio of FeO/RO as shown in the Fig. 2, (a). It is clearly shown, from Fig. 2, (a) that all the chemical compositions of chlorites are plotted in the area of $\text{Al}_2\text{O}_3/\text{R}_2\text{O}_3 \geq 50\%$ (except cronstedtite), and the chlorite area may be divided into as follows.

(a) Mg-Al chlorite area...penninite, leuchtenbergite, sheridanite, grochauite, etc.

(b) Al-Fe''-Mg chlorite area...ripidolite, diabantite, aphrosiderite, etc.

(c) Fe''-Al chlorite area...chamosite.

(d) Fe'''-Al-Fe'' chlorite area...thuringite.

(e) Fe'''-Fe''-Al-Mg chlorite area...delessite, chlororite, clinochlore, prochlorite, etc.

(f) Fe'''-Fe'' chlorite area...cronstedtite.

For the sake of comparison, the chemical compositions of glauconite and celadonite are plotted in the Fig. 2, (a). As well shown from Fig. 2, (a), the plotted points of the chemical compositions of glauconite and celadonite ordinarily fall in the area of $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3 \leq 50\%$.

Conclusion.

The writer tried a generalization of the chemical compositions of fine micas (including glauconite and celadonite) and chlorites and also tried a general expression of these chemical analyses to show some chemical characteristics of these minerals.

*Geological Institute, Faculty of Science,
Tokyo University.*

(12) J. Orcel, *Bull. soc. franç. minéral.*, **50** (1927), 75.

(13) H. Berman, *Am. Mineral.*, **22** (1937), 378.

On the Equilibrium of the Radioactive Elements in the Hydrosphere. III. On the Ratio of Thorium Emanation to Radium Emanation in the Hydrosphere.

By Kazuo KURODA and Yuji YOKOYAMA.

(Received Aug. 31, 1948.)

Introduction.

In the previous paper⁽¹⁾, the occurrence of thorium emanation in the mineral waters of Masutomi was reported by the present authors.

The ratio of thorium emanation to radium emanation in the spring B7 expressed in Mache unit was unexpectedly high and showed the values larger than 10. The authors tried to verify this quite unexpected fact by different methods. The radioactivity of the mineral waters of Masutomi and other famous radioactive springs of Japan was measured and it was found that thorium emanation occurs in many natural waters. The occurrence of thorium emanation was detected and its ratio to radium emanation was determined by the following methods, namely... (1) with the I. M. fontactoscope, (2) with the Lauritsen-type K. Y. fontactoscope, and (3) by the indirect method, in which the radioactivity of the decay products deposited on the negatively charged metals was measured.

I. The Radioactivity Measurements with the I. M. Fontactoscope.

It is not so difficult to obtain the decay curves due to thorium emanation with the I. M. fontactoscope, when the sample water contains considerably high amounts of thorium emanation. However, some technical skill is required, as the half period of thorium emanation is very short, and it disappears if we do not begin the measurements quickly.

The stagnant waters do not contain thorium emanation, and the mineral waters containing large amounts of thorium emanation issue vigorously from the orifice, in most cases directly from the gap in rocks. The samples must be taken very quickly with the injectors of the suitable size, and ejected vigorously in the ionization box of the I. M. fontactoscope. The radioactivity measurement is started as soon as possible. The examples of the decay curves are shown in Fig. 1. a. and Fig. 2. The ratio of the radioactivity of thorium emanation and radium emanation at the time when the sample was taken, is obtained by the extrapolation of the decay curves, as is shown in Fig. 3. Fig. 1. b. shows an example of decay curve of thorium X.

(1) K. Kuroda and Y. Yokoyama, this Bulletin, 21 (1948), 52, 53.

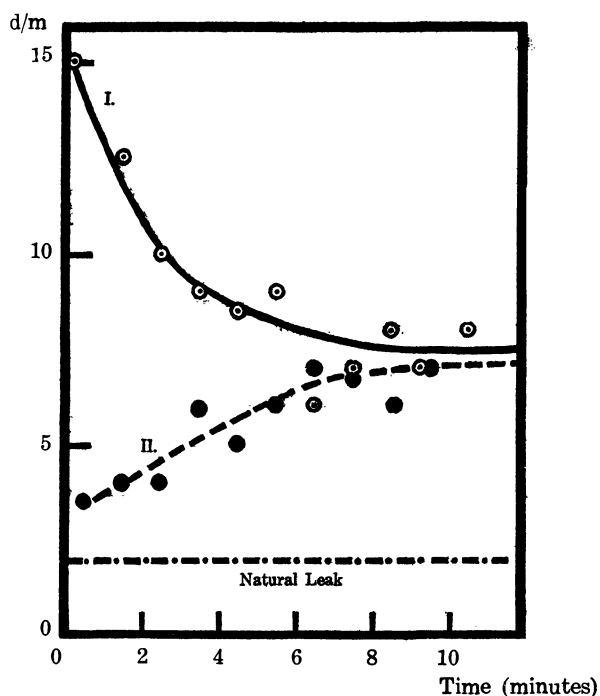


Fig. 1. (a) Decay Curve of Thorium Emanation (I. M. Fontactoscope)
O-T-R, Misasa.

Date Aug. 27, 1948, 15^h 13' 30''

Sample; 100 c.c.

- I. Radioactivity measurement started as soon as possible.
- II. Radioactivity measurement started 5 minutes after the sample was taken with the injector. The decay curve of thorium emanation is not observed.

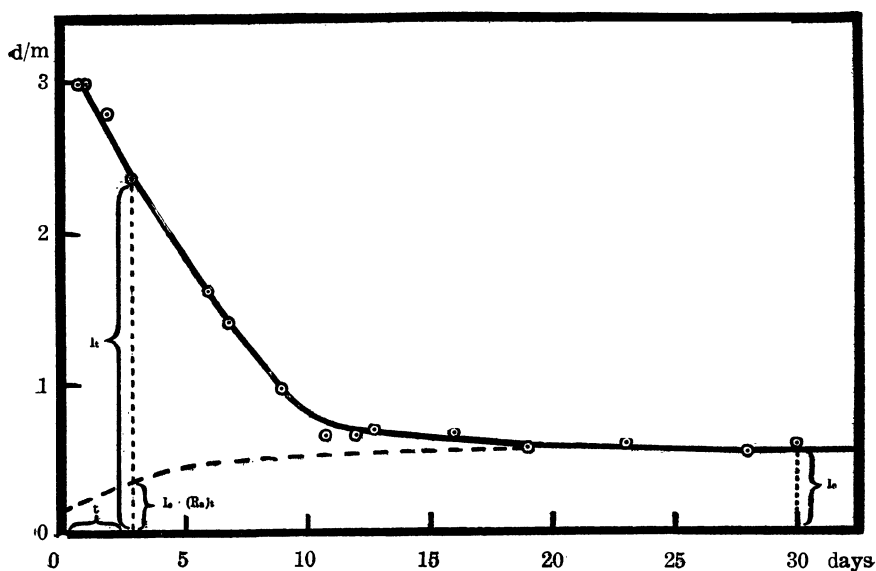


Fig. 1. (b) Determination of the ThX Content and the Ra Content.
Masutomi Spring B7.

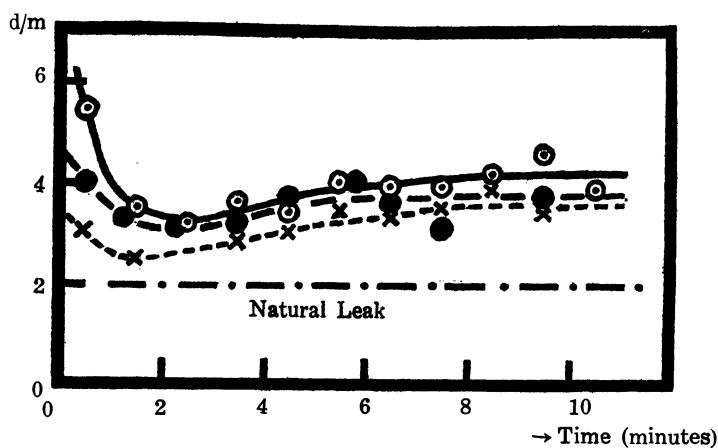


Fig. 2. Decay Curves of Thorium Emanation (I. M. Fontactoscope).
O-K-1, Sekigane.

Date: Aug. 28, 1948

Sample: 50~100 c.c.

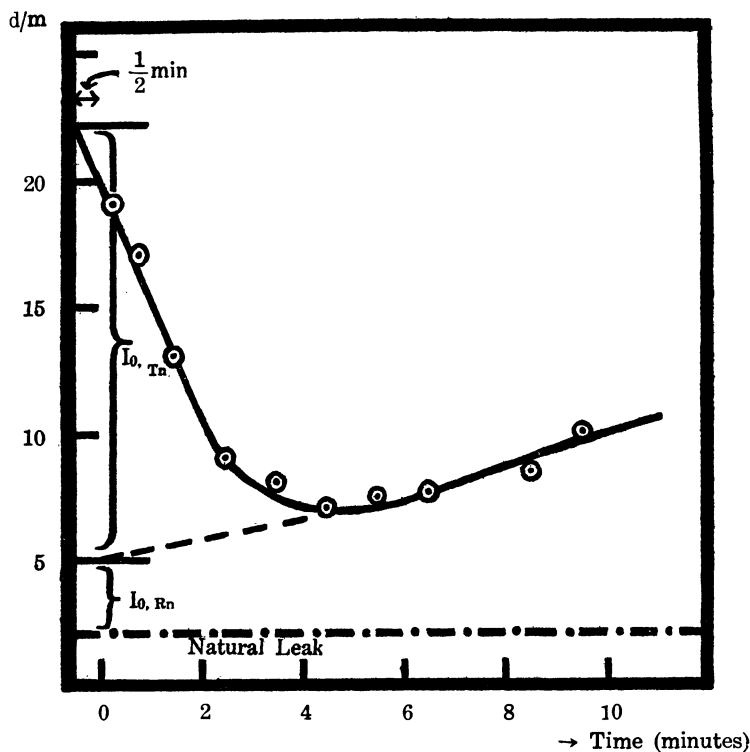


Fig. 3. Determination of the Ratio of Tn/Rn . O-T-R, Misasa. Sample 100 c.c.

II. The Radioactivity Measurements with the Lauritsen-type K. Y.-Fontactoscope.

The decay curves of thorium emanation was also obtained by the radioactivity measurement with the Lauritsen-type K. Y. fontactoscope.

It was rather difficult to determine the ratio of thorium emanation to radium emanation with the K. Y. fontactoscope, compared with the case of the I. M. fontactoscope, as it needed more time to take the sample water into the radon container and to start the radioactivity measurements. However, satisfactory agreements were obtained by these methods. The examples of the decay curves of thorium emanation are shown in Fig. 4.

III. Determination of the Ratio of Thorium Emanation to Radium Emanation by the Indirect Method.

To ascertain the results obtained by the above-mentioned methods, we tried the determination of the ratio of thorium emanation to radium emanation by the indirect method, in which the decay products of thorium emanation and radium emanation are deposited on the negatively charged wires, and the radioactivity is measured with the Lauritsen-electroscope. Fig. 5 shows the apparatus to collect the decay pro-

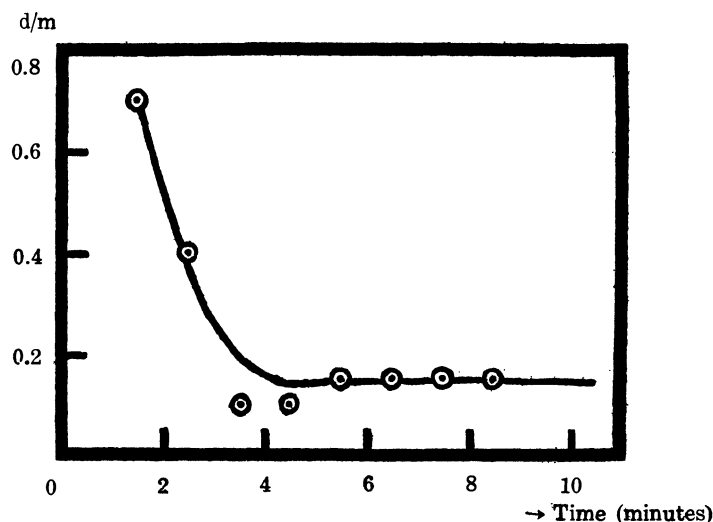


Fig. 4. Decay Curve of Thorium Emanation. (K.Y. Fontactoscope)
The Spring]B7 in Masutomi.

ducts on the wire. For the high voltage battery, the layer built dry batteries of Toshiba Co. were used. The voltage of single battery was 67.5 volts, and one or two batteries were used in each apparatus. This apparatus was exposed overnight at the places very close to the orifice of the springs, and then the radioactivity was measured with the Lauritsen-electroscope.

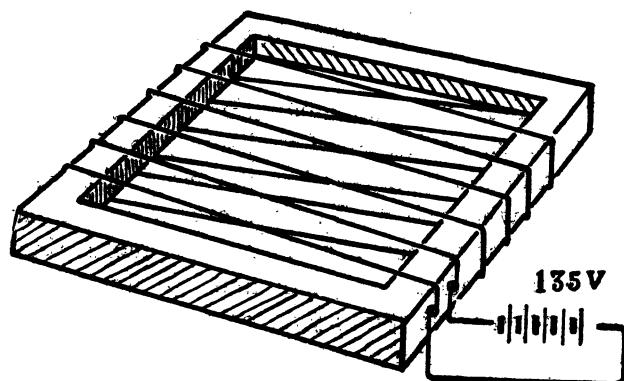


Fig. 5. Apparatus used for collecting the Decay Products of Thorium Emanation and Radium Emanation.

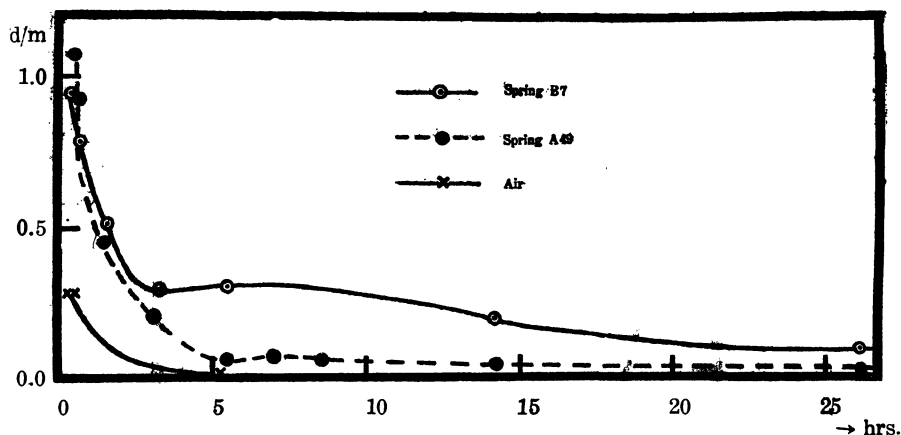


Fig. 6. Determination of the Ratio of Tn/Rn by the Indirect Method.

IV. Results of the Experiments.

The results of the determination of the thorium emanation and radium emanation contents of a number of the hot springs and mineral springs in Japan are shown in Table 1.

Table 1. The Thorium Emanation Content of the Mineral Springs and Hot Springs of Japan.

Masutomi. (Yamanashi Prefecture)

Name	Thorium Emanation Content (Mache)	Radium Emanation Content (Mache)	Apparatus
B7	95	6.27	I.M.
A3	15	2.2	
A3'	15	5.9	
A3''	10	—	
A1	10	—	
A49	absent	about 5000	
Gas from the spring B7	107	19.5	

Ikeda. (Simane Prefecture)

No. 1	absent		K. Y.
No. 3	330	130	

Misasa. (Tottori Prefecture)

O-T-R (Ōhasi-Ryokan)	450	80	I. M.
Matubara	8	26	

Sekigane. (Tottori Prefecture)

O-K-1 (Onseirō-Ryokan)	100	30	I. M.
O-K-2	30	30	
O-U	30	30	
O-N-C	30	30	

Arima. (Hyogo Prefecture)

Tansan-Onsen			
(Small spring)	20-40	ca. 5	I. M.
Sakae-Kōsen	10	ca. 5	

Remark: The thorium emanation content was expressed in Mache unit. It is defined as follows: it is called 1 Thoron-Mache when 0.001 e.s.u. of saturation current is obtained by thorium emanation and its equilibrium amount of thorium A in 1 litre of the sample water.

$$1 \text{ Tn Mache} = 1.52 \times 10^{-10} \text{ Curie/l.}$$

$$1 \text{ g Th unit} = 1.11 \times 10^{-7} \text{ Curie.}$$

In the previous paper, the authors have reported the high content of thorium X and thorium emanation in spring B7 in Masutomi. From the experiments in Masutomi, it was expected that the radioactive springs containing large amounts of thorium X, also contain large amounts of thorium emanation. The thorium X content of the hot springs of Misasa and the mineral springs of Ikeda is not so high compared with that of the mineral springs of Masutomi. Spring No. 3 in Ikeda, which contains the highest amount of thorium X among several springs in Ikeda, was found to contain thorium emanation, but we could not detect the presence of thorium emanation in other springs of Ikeda, as in most cases it was difficult to take the fresh samples from the orifice. The thorium X content of the hot springs of Misasa is much lower than those of Masutomi and Ikeda, and though eight samples containing considerably large amounts of thorium X were measured, thorium emanation was not detected excepting one sample. This was Matubara-no-yu (yu = spring), in which 2.1×10^{-5} g of thorium was found in 1 litre, by Mr. K. Shimokata. The Ōhasi-Ryokan-Soto-Yu showed the highest content of thorium X among the springs of Misasa, but thorium emanation was not detected. Therefore, we concluded that the hot springs of Misasa do not contain the high amounts of thorium emanation, when we visited there for the first time in May of 1948. However, in August of 1948, the radioactivity was

measured with the special-sized counter, and it was found that some springs in Misasa show unexpectedly high radioactivity, whereas their radon or radium contents are not unusual. For example, a spring in the hotel "Ōhasi", called "Tennen-Gankutu-no-yu-Reisen" (O-T-R), showed unexpectedly strong radioactivity when it was examined with the counter. This spring was carefully examined repeatedly with the I. M. fontactoscope, and it was found that the fresh sample of this spring shows high content of thorium emanation. The thorium emanation content of this spring is the highest ever observed in this country and probably in the world.

The hot springs of Sekigane, and the hot springs of Arima were also studied in the summer of 1948, and it was found that the springs containing not so high amounts of thorium X, sometimes contain the considerable amounts of thorium emanation. The authors consider that most radioactive springs contain thorium emanation, but it was not detected by the previous investigators, as the samples were taken from the stagnant springs and as the radioactivity measurements were started very deliberately. The distribution of thorium emanation accompanied by radium emanation in many mineral waters shows that the source of these elements is not so deep under the ground.

The determination of the ratio of thoron to radon by the indirect method was carried out in the summer of 1948, in Masutomi and in Arima. The experimental results are shown in Table 2.

Table 2. The Determination of the Ratio of Thoron to Radon by the Indirect Method.

	Spring B7			Spring A49			In the Air (At the hotel Tuganero)		
Length of the Wire	2 m.			1 m.			2 m.		
Voltage	135 volts			67.5 volts			135 volts		
Beginning of Exposure	19h 10, July 2			19h 00, July 2			19h 00, July 3		
End of Exposure	7h 04, July 3			7h 06, July 3			9h 16, July 4		
Exposed Time	11 hrs 54 m			12 hrs 06 m			14 hrs 16 m		
	t	$I_{\text{obs.}}$	$I_{\text{cal.}}$	t	$I_{\text{obs.}}$	$I_{\text{cal.}}$	t	$I_{\text{obs.}}$	$I_{\text{cal.}}$
	m	d/m		m	d/m		m	d/m	
	26	0.94	0.90	30	1.08	1.06	22	0.27	0.28
	40	0.78	0.82	40	0.92	0.94	27	0.27	0.26
	1h 35	0.52	0.59	1h 26	0.46	0.45	5h 17	0.00	0.00
	3h 20	0.39	0.43	3h 09	0.21	0.12			
	5h 23	0.40	0.38	5h 22	0.06	0.08			
	14h 14	0.19	0.21	6h 59	0.08	0.07			
	27h 33	0.10	0.09	8h 37	0.07	0.06			
	50h 11	0.04	0.02	14h 11	0.04	0.04			
				27h 39	0.01	0.02			
$I_0\text{ThB, C}$	0.49 d/m			0.10 d/m			0.00 d/m		
$I_0\text{RaB, C}$	0.48 "			1.18 "			0.31 "		
$I_{\infty}\text{ThB, C}$	0.99 "			0.20 "			0.00 "		
Thoron/Radon (Curie/Curie)	2.06			0.17			0.00		

In Table 2. $I_0 \text{ ThB, C}$ (= ionization current of thorium B and thorium C at $t = 0$, when the exposure finished) is calculated from the values of ionization current after RaB and RaC have completely disintegrated. The values of ionization current due to ThB and ThC at each time were calculated and these values were subtracted from the observed values of ionization current (I_{OBS}). The values of ionization current due to RaB and RaC are obtained here, and from these values, $I_0 \text{ RaB, C}$ (ionization current due to RaB and RaC at $(t = 0)$) is obtained.

Now, the amount of thorium C formed from thorium emanation in 12 hours is 49.6 % of the equilibrium value, the values of ionization current due to thorium B, C when the activation reached the saturation value ($I_{\infty} \text{ ThB, C}$) are then calculated. The ratio of Tn/Rn is obtained from the ratio of $I_{\infty} \text{ ThB, C} / I_0 \text{ RaB, C}$. $I_{cal.}$ is the calculated value from the values of $I_0 \text{ RaB, C}$ and $I_0 \text{ ThB, C}$. The decay curves and theoretical values showed satisfactory agreements. However, the ratio of Tn/Rn in the atmosphere above the orifice of the springs is obtained by this method, and this value will be different from the ratio of Tn/Rn in the mineral springs. The thorium emanation and radium emanation content of the spring B7 expressed in Curie unit is as follows.

$$\text{Tn} = 144 \times 10^{-10} \text{ Curie/l.}$$

$$\text{Rn} = 20 \times 10^{-10} \text{ Curie/l.}$$

Therefore, the ratio of Tn/Rn in the spring B7 is about 7 expressed in Curie unit. The ratio in the atmosphere on the orifice of the spring B7 is considerably lower than this value, as is shown in Table 2. The reason for this is probably because the half period of thorium emanation is very short and it disintegrates as soon as it issued from the orifice.

The thorium emanation content of the spring A49 was not determined by the direct methods. However it is estimated from the result of indirect determination to be as follows, if we assume that the conditions are same in both springs (B7 and A49).

$$\text{Rn content of the spring A49} = \text{about } 17000 \times 10^{-10} \text{ Curie/l.}$$

$$\text{Tn/Rn in the atmosphere near A49} = 0.17$$

As the ratio $[(\text{Tn/Rn}) \text{ in the air}] / [(\text{Tn/Rn}) \text{ in the water}]$ was 2/7 in the case of the spring B7, the ratio Tn/Rn in the spring water of A49 will be about 0.6.

$$\text{Therefore, the Tn content of the spring A49}$$

$$= \text{about } 10000 \times 10^{-10} \text{ Curie/l.}$$

$$= \text{about } 6600 \text{ Tn-Mache.}$$

$$(\text{Remark ; } 1 \text{ thoron-Mache} = 1.52 \times 10^{-10} \text{ Curie/l.})$$

The determination of the ratio of Tn/Rn was also tried at Arima. In the atmosphere near the orifice of Tansan-Onsen, the decay products o-

thorium emanation were detected, but their radioactivity was very weak, and the radioactivity due to the decay products of radium emanation was not detected.

Table 3. The Determination of the Ratio of Thoron to Radon by the Indirect Method. "Tansan-Onsen" at Arima, Hyōgo Prefecture.

Exposure		19h 40, Sept. 2, ...7h 40, Sept. 3			
Voltage		-135 V			
<i>T</i> (m)	40	1h 42 m	2h 46 m	5h 16 m	10h 0 m
<i>I</i> (d/m)	0.06	0.07	0.07	0.07	0.045

From this, the ratio of Tn/Rn in the atmosphere near the orifice of the "Tansan-Onsen" is considered to be about 10 or larger. Therefore, the ratio of Tn/Rn in the atmosphere at Tansan-Onsen is considerably larger than that of the spring water.

This result is quite different from the result obtained in Masutomi, and further investigation is necessary.

Summary.

The ratio of thorium emanation to radium emanation in natural waters was measured. Following three methods were used: (1) with the I. M. fontactoscope, (2) with the Lauritsen-type K. Y. fontactoscope, and (3) the indirect method, in which the radioactivity of the decay products of thorium emanation and radium emanation is measured with the Lauritsen-electroscope.

It was found that thorium emanation is considerably widely distributed in the mineral springs and hot springs of Japan.

The authors take this opportunity of heartily thanking Prof. Kenjiro Kimura for his kind guidance in the course of this study. The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which our thanks are due.

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On the Equilibrium of the Radioactive Elements in the Hydrosphere. IV. On the Ratio of Thorium X to Radium in the Hydrosphere.

by Kazuo KURODA and Yuji YOKOYAMA.

(Received Aug. 31, 1948.)

Introduction.

In the previous paper⁽¹⁾, the occurrence of thorium X in the mineral waters of Masutomi was reported by the authors. The ratio of thorium X to radium expressed in Curie unit was considerably large in the case of Masutomi. The highest value of this ratio was 10.3 of the spring B7. This ratio was larger than 1 in many springs in Masutomi, and it was considerably larger than the value obtained by Kurbatov in three springs of Gelesnovdsk (0.02 to 0.58). Is this ratio also large in other radioactive springs of Japan or not? The authors have intended to determine the ratio of thorium X to radium in the mineral springs of Ikeda and in the hot springs of Misasa.

I. Determination of Thorium X and Radium.

Radium and thorium X were co-precipitated together with barium sulphate from 1 to 3 litres of the mineral water, and the radioactivity of the powdered precipitate was measured with the Lauritsen-electroscope. The radioactivity diminishes slowly for several days, according to the presence of thorium X. The radioactivity becomes constant after about thirty days and this radioactivity is due to radium. The thorium X content (C_{ThX}) and the radium content (C_{Ra}) were obtained from the equations

$$C_{Ra} = I_e K_{Ra} \quad (1)$$

and

$$C_{ThX} = \frac{I_t - I_e(Ra)_t}{(ThX)_t} \times K_{ThX} \quad (2)$$

where, I_t = observed radioactivity at time t ,

I_e = observed radioactivity at $t = 30$ days,

$(Ra)_t$ = the factor of the radioactivity of radium to calculate the radioactivity at each time,

$(ThX)_t$ = the degree of the disintegration of thorium X in time t ,

K_{ThX} and K_{Ra} = sensitivity of the instrument for thorium X or radium, and their values were as follows:

(1) K. Kuroda and Y. Yokoyama, this Bulletin, 21 (1948), 52.

$$K_{Ra} = 83 \times 10^{-12} \text{ g per div. per min.} \quad (3)$$

$$\text{and} \quad K_{ThX} = 75 \times 10^{-12} \text{ Curie per div. per min.} \quad (4)$$

II. Results.

The results obtained are shown in Table 1 and Table 2. The thorium X contents are shown in two units, their relation being as follows.

$$\text{g Th/l} = 1.11 \times 10^{-7} \text{ Curie/l.} \quad (5)$$

Table 1. The Thorium X and Radium Content of the Hot Springs of Misasa. (May 5, 1948).

Name	Temp. °C	Rn 10 ⁻¹⁰ C/l	<i>I_r</i>	<i>I_e</i>	ThX		
					Ra 10 ⁻¹² g/l	10 ⁻¹² C/l	10 ⁻⁵ gTh/l
(1) Okayama Univ.	61	40	0.31	0.14	12	23	21
(2) Misasa Hotel	58	18	0.36	0.22	18	26	23
(3) Ohasi-Soto-Yu	49	38	1.03	0.14	12	80	72
(4) Matubara	61	70	0.34	0.23	19	25	23
(5) Tennen-Gankutu	43	260	0.28	0.10	8	21	19
(6) Tabakoya	38	560	0.30	0.04	3	24	22
(7) Yamadaku	55	900	0.03	0.03	3	2	2
(8) Hanaya	59	650	0.03	0.03	3	2	2
(9) Akasakiya	42	180	0.02	0.05	4	0.5	0.5

Table 2. The Thorium X and the Radium Content of the Mineral Springs of Ikeda.

Name	Temp. °C	Rn 10 ⁻¹⁰ C/l	<i>I_r</i>	<i>I_e</i>	ThX		
					Ra 10 ⁻¹² g/l	10 ⁻¹² C/l	10 ⁻⁵ gTh/l
No.1	15	480	1.35	0.50	41	108	97
No.2	16.5	380	1.24	0.53	44	98	88
No.3	16	770	1.37	0.50	42	111	100
No.4	13	6100	0.18	0.29	24	9	8
No.5	12.5	8500	0.06	0.07	6	4	4
Oku-no-yu	22	(20)	0.64	0.25	21	50	45

Table 1 and Table 2 show that the ratio of thorium X to radium is also large in the mineral springs of Ikeda and the hot springs of Misasa. The highest value was 8.0 in the spring water of Akasakiya in Misasa. The following rules were found in Ikeda and in Misasa, namely: (1) the higher the water temperature and the larger the amount of flow, the larger is the ratio of ThX/Ra, and (2) the larger the radium content and the smaller the radon content, the larger is the thorium X content. These tendencies are quite similar to those obtained in Masutomi, but they are not so clear compared with the case of Masutomi. It is probably because the springs issue from the bottom of the bath, and we sometimes used stagnant waters. The ratio of thorium X to radium in these mineral springs are summarized in Table 3 and Table 4.

Table 3. The ThX/Ra Ratio in 25 springs of Masutomi.

ThX/Ra	<1	1-2	2-4	4-6	>6
Number of springs	7	4	5	5	2

Table 4. The ThX/Ra Ratio in 15 Springs of Misasa and Ikeda.

ThX/Ra	<1	1-2	2-4	4-6	>6
Number of springs in					
Misasa	3	3	1	0	2
Ikeda	2	0	4	0	0

Summary.

The thorium X and radium contents of mineral springs of Ikeda and the hot springs of Misasa were estimated. The ratio of thorium X to radium in these springs was considerably larger than that obtained by Kurbatov in Gelesnovdsk. The relation between the ratio of thorium X and radium, and water temperature, radium content, radon content, etc., was quite similar to that found in Masutomi.

The authors take this opportunity of heartily thanking Prof. Kenjiro Kimura for his kind guidance in the course of this study.

The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which our thanks are due.

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Separation of the Components of Atmospheric Salt and their Distribution.

By Ken SUGAWARA, Shinya OANA and Tadashirô KOYAMA.

(Received October 2, 1948.)

Introduction. It is a wellknown fact that the splash of sea water is carried up into the air and plays an important role as the primary source of the salt in rain and snow.

Now, it is worth attention that the salt in rain and snow differs so much in composition from sea salt that the ratios $Mg:Cl$ and $SO_4:Cl$ of such salt are larger than those of sea water as shown by H. Lipp⁽¹⁾ of the fog from Mt. Sonnblick and by Y. Miyake⁽²⁾ of Japanese rain.

As the cause of this difference, we can assume that, by evaporation, there occurs a partial crystallization on the suspending particles of sea water in the air with the production of at least two kinds of daughter particles; the one, hygroscopic in nature and consisting mainly of sodium and chloride, is unstable and falls down earlier from the air, while the other, crystalline in nature and consisting mainly of magnesium and especially of calcium and sulphate, is stable and keeps to remain longer in the air. It is quite natural that these circumstances lead to the relative concentration of the latter kinds of components in the air, which explains well the observations by Lipp and Miyake.

Now, be such a view right, it can be expected that there may occur a distribution of the atmospheric salt with such a variation in composition that the ratios of magnesium, calcium or sulphate to sodium or chloride increase horizontally as we get along from sea coast towards inland, and also we may find a similar distribution vertically as we get higher from sea level upwards.

In the next, be such a variation in salt distribution actually shown, a second question will arise; how does the selective falling down of the unstable components occur?

The present paper deals with these two kinds of problems and answers them by the chemical study of the precipitation, the atmospheric salt itself and also of the salt caught by pine needles on their surfaces from the air.

Horizontal Distribution of the Components of Sea Salt in the Air from Sea Coast towards Inland. Observation was carried out at three stations; the one next sea beach, Sugashima-Island in Ise Bay, the second Nagoya (Higashiyama), 4 km. receding from the head of Ise Bay, and the third the most receding place, Matsumoto, Nagano Pref., 180 km. from

(1) H. Lipp, *Jahresber. des Sonnblickvereins*, 1931, 27, Wien.

(2) Y. Miyake, *J. Meteorol. Soc. Japan*, II, 17 (1939), 20.

the Pacific coast and some 90 km. from Japan Sea.

On more than one hundred samples of rain and snow, taken during 1946–1947, chemical analyses were carried out and their ratios Na:Cl, Mg:Cl, Ca:Cl, and SO₄:Cl determined, the result of which (columns A of Table 1) tells that, as was expected above, the ratios Ca:Cl, SO₄:Cl and also Mg:Cl increase markedly as it recedes into inland.

Table 1.

Ratio in equivalent	Sea water	Rain (A)			Washings of pine needles (B)		
		Sugashima	Nagoya	Matsu-moto	Sugashima	Nagoya	Matsu-moto
Na/Cl	0.850	0.85	0.90	0.63	0.83	0.85	2.1
Mg/Cl	0.196	0.23	0.31	0.99	0.22	0.27	1.4
Ca/Cl	0.038	0.25	0.31	6.84	0.09	0.55	3.8
SO ₄ /Cl	0.103	0.35	0.33	2.25	0.17	0.72	2.7

A similar relation is also shown in the salts which were caught by pine needles.

Studies along this line were made as follows: a certain twig was chosen among pine woods and their needles were washed thoroughly with distilled water. After a few days, during which there fell no precipitation, the needles were washed again and the salt, caught by them on their surfaces during the period, was gathered in the washings, of which chemical analyses were carried out.

The Columns B of Table 1 give the result. The increase of Ca:Cl, SO₄:Cl and Mg:Cl is found also here and more evidently.

Vertical Distribution of the Components of Sea Salt in the Air from Sea Level upwards. This kind of distribution is shown by the comparison of the three different kinds of meteorological water-substances; the ordinary rain from 500–1000 m., the fog-ice from the summit of Mt. Fuji (3376 m. high) and the waters of thunderstorm, gathered in Nagoya and in Utsunomiya, Tochigi Pref., the latter kind of water being said to be given rise to at a height of 4–15 km.

The result (Table 2) shows that the ratios Ca:Cl, SO₄:Cl and Mg:Cl grow larger with height, proving a denser distribution of calcium, sulphate and also magnesium relatively to other components in the height.

Table 2.

Ratio in equivalent	Ordinary rain	Fog-ice from the summit of Mt. Fuji	Thunderstorm
Na/Cl	0.90	1.09	2.43
Mg/Cl	0.31	0.40	0.63
Ca/Cl	0.31	1.90	2.19
SO ₄ /Cl	0.33	1.00	3.24

Ways in which Unstable Components fall down earlier. As to the question, by what processes the unstable components fall down earlier, we can give an answer that there are at least two different kinds of way;

the one the selective washing down by rain and the other selective capturing by various occupants extruding themselves from the earth surface (for examples, shrubs, woods or artificial edifices, etc.) on which some explanations must be given below.

(a) **Selective Washing by Rain.** This action of rain can be shown from two different sides.

(1) First we can show it by the direct comparison of the composition of atmospheric salt at a certain place to that of the rain which falls there. We can mention one example of Nagoya (Table 3, A, B) in which we find that the values $\text{Ca}:\text{Na}$ and $\text{SO}_4:\text{Na}$ are smaller in rain than in the air itself, while the value $\text{Mg}:\text{Na}$ remains practically constant. The relation is quite comprehensible when we assume that rain prefers sodium, magnesium and chloride to calcium and sulphate in the course of its washing action.

Table 3.

Ratio in equivalent	Atmospheric salt (A)	Salt of rain (B)	Salt caught by pine needles (C)
Ca/Na	1.36	0.34	0.65
Mg/Na	0.30	0.33	0.31
SO_4/Na	0.68	0.38	0.60

(2) The second way which proves the selective washing by rain is indirect and needs a somewhat precise explanation.

First we must make clear the relation between the chloride concentration of rain and the amount of its precipitation. The relation is shown by Fig. 1, drawn from the data of 60 kinds of rain in Nagoya, where

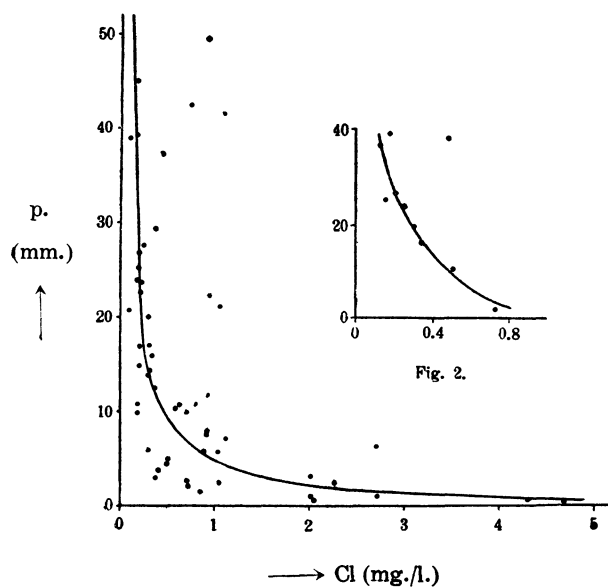


Fig. 1.

abscissae denote chloride concentration and ordinates the amount of precipitation.

As it is evident, all the values, except ones with particular nature such as ones of thunderstorm, lie practically on a line of hyperbolic form, expressed by $\text{Cl mg./l.} = 4.2/p \text{ mm.}$ The relation is far more evident in the case of rains in rainy season, when practically even meteorological conditions keep to prevail. (Fig. 2)

How can we understand the relation here found?

May we liken it to the case in laboratory where a certain amount of solute is treated with a sufficient or an insufficient amount of solvent?

A dilute solution will be obtained in the former case. The rain of a large precipitation poor in chloride might be likened to this, while another case, where only an insufficient amount of solvent is available, corresponds naturally to a rain of a smaller precipitation rich in chloride.

Now let us go further to imagine a case, where a mixture of a number of solutes, differing in solubility, be treated by solvent. Be the amount of solvent enough in this case, all the mixture will go into solution, while be it insufficient, dissolution will be incomplete and partial, components with larger solubilities going into solution first, and ones less soluble being left unattacked. Can we find the same relation also in the case of rain? Speaking more concretely, can we distinguish two kinds of rain, the one a dilute rain with larger ratios of Ca:Cl and $\text{SO}_4:\text{Cl}$, i.e., one the salt composition of which is nearer to that of atmospheric salt, and the other a rather concentrated one with smaller values of Ca:Cl and $\text{SO}_4:\text{Cl}$, which seems to have dissolved the salt in the air partially?

This is actually the case. In order to show it, we had better to begin with examples (Table 4). We may choose the rain of Sept. 13th, 1946 as an example of a smaller precipitation rich in chloride and that of Feb. 20th, 1947 as one of a larger fall poor in chloride.

Table 4.

Amount of precipitation	Sept. 13th, 1946 4.2 mm.	Feb. 20th, 1947 10.3 mm.
Cl	0.121 milliequiv./l.	0.0273 milliequiv./l.
Na	0.105 "	0.0195 "
Ca	0.0068 "	0.0163 "
Mg	0.0283 "	0.0073 "
SO ₄	0.0273 "	0.0142 "
Na/Cl	0.872	0.696
Ca/Cl	0.056	0.597
Mg/Cl	0.233	0.267
SO ₄ /Cl	0.226	0.521

In comparing the ratios of the salt components of these two kinds of rain, we find, as expected, that, while Na:Cl and Mg:Cl remain not differing much, difference is so marked of Ca:Cl and $\text{SO}_4:\text{Cl}$ that the values of the dilute Sept. 13·rain attain 2–10 times as high as those of the concentrated Feb. 20th one.

Now the relation is no accidental one, particular to the examples cited, but a more general one. This can be shown by Fig. 3 in which, referring to the chloride values (abscissae), the corresponding ones of sodium, magnesium, calcium and sulphate (all expressed in milliequivalent/l.) are taken as ordinates and four kinds of lines, Na-Cl, Mg-Cl, SO_4 -Cl and Ca-Cl are drawn.

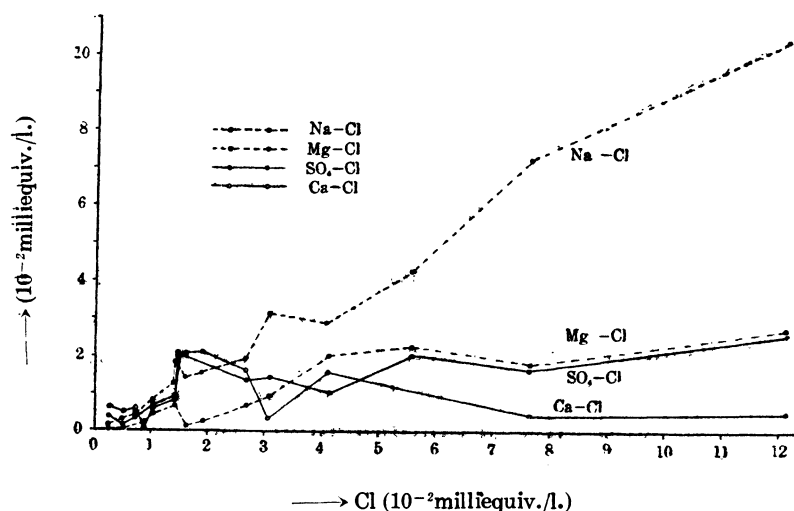


Fig. 3.

The perusal of the lines tells us much of the different behaviours of the individual components in their course of dissolution into rain, but here we must confine ourselves to focus our attention solely upon the point now in question. Then the primary point to be considered is that in contrary to the Na-Cl line, which runs with a gradient practically constant throughout the entire range, the lines SO_4 -Cl and Ca-Cl start with rather acute gradients and then immediately tend to run along rather horizontally.

These circumstances can be taken to indicate that, when the amount of rain is small, among the salt components in the air, it chooses more soluble ones, such as sodium, chloride or magnesium and washes down them first, with the production of a rather concentrated water whose content of calcium and sulphate is relatively small, and on the other hand, when the amount of water is sufficient, or when the washing action keeps to continue longer, the action comes over to less soluble calcium and sulphate, thus yielding a water dilute but relatively rich in the latter components.

Further it must be added that the figure tells that such is the case of wide and general occurrence.

(b) **Selective Capturing by various Occupants extruding themselves on the Earth Surface.** This is shown by the comparison of the

composition of the atmospheric salt and that of the captured by pine needles. The columns A and C of Table 3 show it. As it was shown in the comparison of rain and the atmospheric salt itself, we find also here that Ca:Na and SO₄:Na show smaller values in the pine salt than the atmospheric one, while Mg:Na remains to be practically constant.

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**Studies on the Selenium Barrier Layer Photoelement. V.⁽¹⁾
Photocurrent, Photopotential and Cell Resistance
in Relation to the Intensity of Illumination,
and Dependence of the Photocurrent
and the Photopotential on
the Temperature.***

By Masao TOMURA.

(Received November 10, 1948.)

Introduction. Until now mechanism of a cuprous oxide barrier layer cell has been explained qualitatively by N.F. Mott⁽²⁾ and one of a selenium barrier layer cell by M. Tomura,⁽³⁾ but there have been no quantitative studies on the relations of photocurrent, photopotential and cell resistance to the intensity of illumination, and on the dependence of the photocurrent and the photopotential on the temperature. For more detailed studies on the mechanism of cell and the applications of it, the establishment of the quantitative relations of the above quantities is desired.

Mechanism of the Barrier Layer Photoeffect of the Selenium Cell. According to Tomura⁽³⁾ it is the barrier layer which is formed at the contact between the selenium semiconductor and the translucent metal electrode that plays an important rôle in the barrier layer photoeffect. When both elements are in contact, if the Fermi surface of the metal is higher than the thermodynamic potential of the semiconductor, the electrons in the metal go into the empty impurity centres of the selenium

(1) The preceding reports are in *Proc. Toshiba Lab.*, **18** (1943), **19** (1944).

(2) N.F. Mott, *Proc. Roy. Soc. (A)*, **171** (1939), 281.

(3) M. Tomura, *Proc. Toshiba Lab.* **18** (1943), 523.

* Read at the Research Meeting of Electronic Emission, Tokyo (Jan. 1948.)

which is an abnormal semiconductor and consequently the energy level of the selenium in the neighbourhood of the contact becomes like that shown in Fig. 1.

In this way, there occurs a so-called barrier layer of 10^{-5} ~ 10^{-6} cm. thick in which exists internal field of order of 10^5 v./cm. When the incident

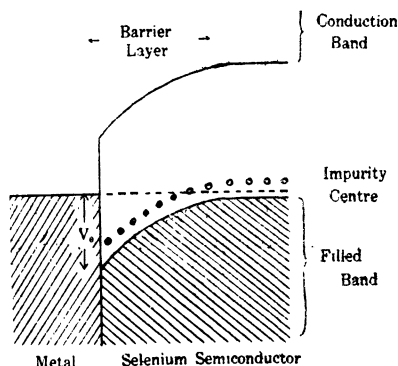


Fig. 1. Potential energy of an electron at the contact between a metal and selenium semiconductor.

light falls through the surface metal electrode on to the barrier layer, photoelectrons are freed owing to the internal photoeffect of selenium. Then they and their holes are accelerated by the internal field through the barrier layer and photocurrent is observed in the external circuit. It is only the photoelectrons and photo-positive-holes (holes of photoelectrons) which are created in the barrier layer that cause the external photocurrent, and the quantum yield is nearly one for the light absorbed in the barrier layer.

On the other hand, when a barrier layer is formed by the contact of a metal with selenium semiconductor, the rectifying action can be detected always, which is explained semiquantitatively by the Mott's theory.⁽⁴⁾

Equivalent Circuit of the Selenium Barrier Layer Photoelement. The above mechanism can be represented by an equivalent circuit which is shown in Fig. 2. Namely, the parallel circuit of the source of the photocurrent Q and the rectifying internal resistance R_i is combined in series with the resistance of electrode metal R_f , the spreading resistance of selenium semiconductor R_s and the external resistance R_e .

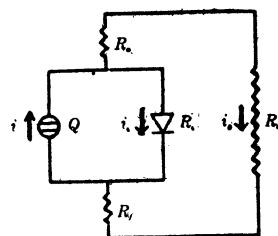


Fig. 2. Equivalent circuit of a selenium barrier layer photoelement.

If photons are absorbed in the cell, photoelectrons and photopositive holes cause the primary photocurrent i in Q by the acceleration of the internal field of the barrier layer, making the external current i_e in the total external resistance $R = R_f + R_s + R_e$. The voltage drop $i_e R$ owing to the flow in the external circuit is impressed upon R_i , so the rectifying current i_i flows through R_i as indicated by an arrow in the figure. This current is a stream of positive holes, being equivalent to the easy flow of the rectification of the cell. As the current i_i cancels a part of the original current i , the remainder forms the external current i_e . Then we have $i - i_i = i_e$.

In this case i is proportional to the intensity of illumination; but i_i and i_e are influenced by R_e and the temperature, because R_i depends on the voltage which is applied on itself and the temperature. This is the

(4) N. F. Mott, *Proc. Roy. Soc. (A)*, **171** (1939), 27.

cause of complicated behaviour of the photocurrent, photopotential and cell resistance under different conditions.

Theoretical Calculations. Since the primary photocurrent i is proportional to the intensity of illumination I ,

$$i = \alpha I \dots\dots\dots (1)$$

is obtained. Here α is a constant. From the above section, furthermore, the next relation exists.

$$i = i_i + i_e \dots\dots\dots (2)$$

Since the selenium photoelement has a barrier of pure contact, we may apply Mott's theory to the barrier of pure contact which has a parabolical internal potential. Then we obtain⁵⁾

$$\left. \begin{aligned} i_i &= \frac{2\sqrt{V_0} \sqrt{V_0 - V}}{\rho_\infty} (e^{\frac{eV}{kT}} - 1) \\ \rho_\infty &= \frac{d}{evn_0} \\ n_0 &= 2 \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} e^{-\frac{eV_0}{kT}} \end{aligned} \right\} \dots\dots\dots (3)$$

where V_0 is the contact potential difference between the metal and the semiconductor, V the voltage impressed on R_i , e the charge of an electron, k the Boltzmann constant, T the absolute temperature, d the thickness of the barrier layer, v the mobility of a positive hole, m the mass of an electron and h the Planck constant.

For the case of a cuprous oxide backwall cell having a constant internal field in its barrier layer which was treated by Mott, the next formula is to be taken instead of the equation (3).

$$i_i = \frac{V_0 - V}{\rho_\infty} (e^{\frac{eV}{kT}} - 1) \dots\dots\dots (3')$$

The equations (3) and (3') hold only in the range of $V < V_0$ and V cannot exceed V_0 even if I becomes large. It is the easy flow of the rectifying current that goes into our problem, so the image force effect can be neglected.

From the equations (1), (2) and (3), we obtain

$$\left. \begin{aligned} \alpha I &= i_e + \frac{2\sqrt{V_0} \sqrt{V_0 - V}}{\rho_\infty} (e^{\frac{eV}{kT}} - 1) \\ V &= i_e R = i_e (R_f + R_s + R_e) \end{aligned} \right\} \dots\dots\dots (4)$$

(5) R. Kubo, private communication.

The equation (4) represents the general relations between the photocurrent, photopotential and cell resistance, and their dependence to the intensity of illumination as well as to the temperature.

(a) Photopotential. Photopotential V_p is defined usually as the open potential of the cell, so V_p is given by making $i_e=0$ in (4). Namely,

$$aI = \frac{2\sqrt{V_0} \sqrt{V_0 - V_p}}{\rho_\infty} (e^{\frac{eV_p}{kT}} - 1) \dots\dots\dots (5)$$

When $eV_p \ll kT$, or I is small and T is large, we have

$$aI = \frac{2V_0}{\rho_\infty} \frac{eV_p}{kT} \dots\dots\dots (6)$$

from (5), because the condition $V \ll V_0$ holds. Then V_p is proportional to I .

In the range of $eV_p \gg kT$, (5) becomes

$$aI = \frac{2\sqrt{V_0} \sqrt{V_0 - V_p}}{\rho_\infty} e^{\frac{eV_p}{kT}} \dots\dots\dots (7)$$

so V_p is proportional to $\log I$.

(b) Photocurrent. If we put $V=i_e R=i_e (R_f + R_s + R_e)$ into (4), the relations between i_e and I or R are obtained. Especially for the case of $eV \ll kT$,

$$aI = i_e \left(1 + \frac{2eV_0 R}{\rho_\infty kT} \right) + \dots\dots$$

namely,

$$i_e = \frac{aI}{1 + \frac{2eV_0 R}{kT \rho_\infty}} \dots\dots\dots (8)$$

is obtained.

Usually i_e for $R_e=0$ is called the short circuit photocurrent, but since R_f and R_s is finite, we cannot obtain the theoretical short circuit current even though we make use of the Campbell Freeth circuit. R_f and R_s are so small compared to the usual external resistance that the practical short circuit photocurrent i_{es} is obtained as

$$i_{es} = aI \dots\dots\dots (9)$$

by introducing $V=0$ into (4). This equation is right so long as the condition $V=i_e(R_f + R_s) \approx 0$ holds.

(c) Cell Resistance. So called cell resistance is defined as the ratio

of photopotential to the short circuit current at a given intensity of illumination. From (5) and (9),

$$i_{es} = \frac{2\sqrt{V_0}\sqrt{V_0-V_p}}{\rho_\infty} (e^{\frac{eV_p}{kT}} - 1) \dots\dots\dots (10)$$

is obtained. So R_i is given by the next equation.

$$\frac{1}{R_i} = \frac{i_{es}}{V_p} = \frac{2\sqrt{V_0}\sqrt{V_0-V_p}}{\rho_\infty V_p} (e^{\frac{eV_p}{kT}} - 1) \dots\dots (11)$$

The above defined cell resistance is the ratio of two quantities of two different physical states, so it has no real physical meaning. But as (11) shows, it is a formal easy flow resistance of the barrier layer onto which the photopotential V_p is impressed.

(d) Dependence of the Photopotential on the Temperature. If we consider a case of $eV_p \ll kT$, we can derive the next equation from (6).

$$V_p = \frac{\alpha I}{\beta} \frac{e^{\frac{eV_0}{kT}}}{T^{\frac{1}{2}}} \dots\dots\dots (12)$$

where

$$\beta = 4 \left(\frac{2\pi mk}{h^2} \right)^{\frac{3}{2}} \frac{e^2 v V_0}{kd}$$

Namely, V_p decreases exponentially with T .

And then, in the region where $e^{\frac{eV_p}{kT}} \gg 1$ and $V_p/V_0 \ll 1$ hold, we can derive

$$V_p = V_0 + \frac{kT}{e} \log \frac{\alpha I e}{\beta k T^{\frac{3}{2}}} \dots\dots\dots (13)$$

from (5) approximately. This equation means that V_p decreases when T increases, because $\log(\alpha I e / \beta k T^{\frac{3}{2}})$ must be negative from (5), that is to say, T must be larger than a definite value.

(e) Dependence of the Photocurrent on the Temperature. In the same manner as (d), we can derive the relations between i_e and T , by introducing $V = i_e R$ into (4) and (8). The result is that i_e decreases when T increases.

At low temperatures we must consider variations of α and v with temperature, and the tunnel effect of positive holes through the barrier layer, making increase of i_i . Thus we cannot gain characteristics of photopotential and photocurrent at low temperatures from (3).

Discussions of the Results. In general the results of the preceding sections can be confirmed by experiments.⁽⁶⁾ The equation (3) which we

(6) B. Lange, "Die Photoelemente und ihre Anwendung", Leipzig (1936).

take as the basis of our calculation is purely theoretical, yet it explains quantitatively the characteristics of the selenium cell, although it fails to explain rigorously the minor details of the experimental results. This fact is attributed to the non-uniform nature of the barrier layer which is found also in the case of the selenium rectifier.

As for the cuprous oxide frontwall cell, since its barrier layer is considered as a pure contact of a metal and a cuprous oxide semiconductor and has a parabolical internal field, the results of the above calculations can be applied just in the same way. But the cuprous oxide backwall cell has a barrier layer of a constant internal field,⁽⁴⁾ so we must take up the equation (3') instead of (3). In this case the results are not very different from the above results.

At very low temperature, as above mentioned, corrections must be added. On the other hand, at higher temperatures than room temperatures, selenide formation takes place in the barrier layer as the author has pointed out,⁽⁷⁾ so care must be taken in the experiments at the higher temperatures.

Conclusion. By clearing up the relations between the barrier layer photoeffect and rectification of a barrier layer and by applying the Mott's theory of a barrier layer rectifier, the general formula of the relations between the physical quantities of the barrier layer photoelement are derived and their features explained.

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(7) M. Tomura, *Proc. Toshiba Lab.*, **19** (1944), 206.

On the Chemical Compositions of the Eruptives of Volcanoes in New Britain, Pacific Ocean.

By Yasuo MIYAKE and Yoshio SUGIURA.

(Received November 12, 1948.)

We have carried out the chemical analysis of lava, lapilli and volcanic sand ejected from the volcano group near the city of Rabaul in New Britain (Bismarck Archipelago).

These volcanoes are Mt. Tavurvur, Mt. Kombiu and Mt. Baluan. Samples for the chemical analysis were collected by Mr. Kizawa, a seismologist of the Central Meteorological Observatory of Japan, in 1942.

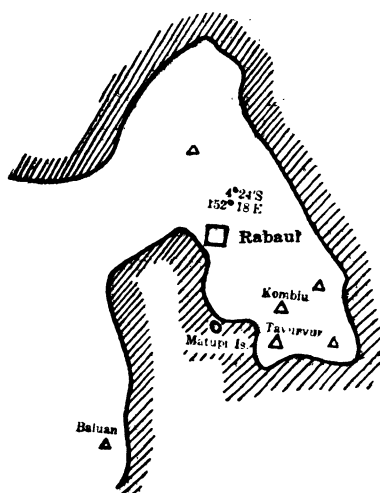


Fig. 1. The volcano group near the city of Rabaul

The present conditions of these volcanoes are as follows. Mt. Tavurvur exploded in 1937, and its volcanic activity has continued until the present day. Mt. Baluan erupted after the explosion of Mt. Tavurvur in 1937, but it is in dormant state now. Mt. Kombiu has two craters. The old one is called Rabalankaia which has been dormant since 1870, and the other is Palagiagia which was active till recent days.

The chemical compositions of the following seven samples have been studied.

Table 1.

No.	Name of Mountain.	Kind.	Colour, etc.	Place of Collection.
1.	Mt. Tavurvur.	Lapilli.	Blackish violet, pumiceous.	East side.
2.	do.	Sand	Pale reddish brown.	do.
3.	do.	Lapilli.	Like No. 1.	Top
4.	Mt. Baluan.	Lapilli.	Black.	do.
5.	Mt. Kombiu. (Rabalankaia)	Lapilli.	Black.	Wall of the crater.
6.	do.	Lava sand.	Blackish blue.	Bottom of the crater.
7.	do. (Palagiagia)	Lava.	Black.	Unknown.

In Table 2 and Table 3, the results of chemical analysis are given.

Table 2.

Chemical Compositions of the Eruptives from Mt. Tavurvur.

	No. 1.	No. 2.	No. 3.	Mean.
Si O ₂	48.47 %	46.65 %	48.34 %	47.82 %
Ti O ₂	0.77	1.17	0.85	0.93
Al ₂ O ₃	18.81	20.11	17.75	18.89
Fe ₂ O ₃	3.70	4.49	4.64	4.28
Fe O	6.39	5.96	6.73	6.36
Mn O	0.19	0.28	0.23	0.23
Mg O	5.68	5.33	5.35	5.45
Ca O	12.75	11.40	11.96	12.04
Na ₂ O	1.94	2.19	3.19	2.44
K ₂ O	0.53	0.64	0.49	0.55
P ₂ O ₅	0.25	0.31	0.75	0.44
H ₂ O ⁺	—	0.01	—	—
H ₂ O ⁻	0.23	0.50	0.17	0.30
Total.	99.71	99.04	100.45	99.73

Table 3.
Chemical Compositions of the Eruptives from
Mt. Baluan and Mt. Kombiu.

	No. 4.	No. 5. & No. 6.	Mt. Baluan		
	No. 7.		Mt. Kombiu (Rabalankaia)		
	No. 4	No. 5.	No. 6.	No. 7	Mean.
Si O ₂	61.75 %	59.75 %	60.80 %	59.40 %	60.42 %
Ti O ₂	1.08	0.87	0.95	0.90	0.95
Al ₂ O ₃	14.44	14.00	15.50	14.81	14.69
Fe ₂ O ₃	3.05	2.06	2.51	3.30	2.73
Fe O	3.67	5.01	3.57	3.93	4.05
Mn O	0.12	0.09	0.14	0.15	0.13
Mg O	1.52	2.61	1.62	2.12	1.97
Ca O	7.53	9.16	8.01	9.61	8.58
Na ₂ O	3.55	3.98	3.48	3.27	3.57
K ₂ O	1.88	1.91	1.82	2.33	1.99
P ₂ O ₅	0.73	0.54	1.00	0.95	0.81
H ₂ O ⁺	0.05	0.21	0.29	0.11	0.17
H ₂ O ⁻	0.08	0.07	0.27	0.02	0.11
Total	99.45	100.26	99.93	100.90	100.17

From these results we can find a good similarity among the composition of three samples collected on Mt. Tavurvur. In the other hand, eruptives from Mt. Baluan and Mt. Kombiu have almost the same composition which distinctly differs from those of the eruptives from Mt. Tavurvur. Eruptives from Mt. Tavurvur have low silicic acid content (smaller than 50%) and contain more aluminium, iron, manganese, calcium and magnesium, and less alkalis than those from the other two volcanoes, therefore, they may be called basaltic. On the contrary, eruptives from Mt. Baluan and Mt. Kombiu have comparatively high silicic acid content (almost 60%), and they are quartz-andesitic.

There are old data of chemical analysis of lava and pumice in New Britain by A. Liversidge⁽¹⁾ (1883), which are fairly different from our results. But, as H. S. Washington pointed out, the content of magnesium is too small and manganese is too high in his data and these are not probable. It is of interest to compare the chemical compositions of the eruptives of volcanoes in New Britain with the eruptives of famous volcanoes in Japan. Mean values of those of Mt. Tavurvur and Mt. Kombiu and other data of eruptives in Japan are given in Table 4.

(1) H. S. Washington, "Chemical Analysis of Igneous Rocks," p. 250, 429 Washington, D. C. (1903).

Table 4.

	Tavurvur	Kombiu	Aso ⁽²⁾	Fuji ⁽³⁾	Fuji ⁽⁴⁾
Si O ₂	47.82 %	60.42 %	53.92 %	49.31 %	57.87 %
Ti O ₂	0.93	0.95	0.85	0.60	0.82
Al ₂ O ₃	18.89	14.69	18.67	19.86	17.80
Fe ₂ O ₃	4.28	2.73	2.69	3.93	3.07
Fe O	6.86	4.05	5.93	6.43	5.31
Mn O	0.23	0.13	0.14	0.22	0.20
Mg O	5.45	1.97	3.80	5.11	2.63
Ca O	12.04	8.58	9.27	11.03	6.80
Na ₂ O	2.44	3.57	2.90	1.97	3.52
K ₂ O	0.55	1.99	1.86	0.60	1.43
P ₂ O ₅	0.44	0.81	0.27	0.16	0.27
H ₂ O ⁺	—	0.17	0.21	0.51	0.91
H ₂ O ⁻	0.30	0.11	—	—	—
Total	99.73	100.17	100.51	99.73	100.63

In this Table we can see the resemblance between the chemical compositions of the eruptives of the volcano group near the city of Rabaul and those of Mt. Fuji.

Meteorological Institute, Tokyo, Japan.

(2) Y. Miyake and K. Mayama, *J. Met. Soc. Jap.* Ser. II. **16** (1938), 95.

(3) I. Iwasaki, *J. Chem. Soc. Jap.*, **58** (1937), 487.

(4) I. Iwasaki and M. Ikawa, *ibid.*, **59** (1938), 1175.

The Addition of Hydrogen Bromide to Cinnamic Acid and the Oxygen Effect.⁽¹⁾

By Osamu SIMAMURA and Makoto TAKAHASHI.

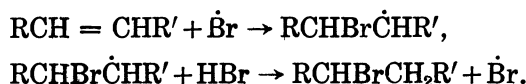
(Received November 16, 1948.)

The problem of the oxygen effect in the addition of hydrogen bromide to ethylenic compounds, manifesting itself in the reversal of the direction of addition expected from Markownikoff's rule, appears to have been settled so far as its general character is concerned.⁽²⁾ The active agents which cause the abnormal addition have turned out to be bromine atoms produced from hydrogen bromide under relevant experimental conditions.

(1) Presented at the 68th Annual Meeting of the Chemical Society of Japan in Tokyo, October 18, 1946.

(2) For reviews of the subject see Y. Urushibara, *Kwagakusoho*, **6** (1944), 185; F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

A bromine atom adds to the ethylenic bond to produce a free radical containing bromine, and this reacts with hydrogen bromide yielding a molecule of the final addition product and another bromine atom, the latter in turn attaching itself to another molecule of the ethylenic compound to reproduce the free radical:



Thus a chain reaction occurs, and in each cycle one molecule of the abnormal addition product is produced. However, concerning essential factors deciding the position of attack by the bromine atom and hence the orientation of hydrogen bromide a consensus of opinion has not yet been attained. Furthermore, in such cases as crotonic^(3,4,5) and cinnamic⁽⁴⁾ acids no reversal has ever been observed, the products under the oxygenic or peroxidic condition being identical with those under the normal condition, and with regard to the mechanism of the phenomena several theories have been set forth by various workers.

The investigation on the addition of hydrogen bromide to crotonic acid reported from this Laboratory⁽⁵⁾ was a contribution to elucidation of these moot questions. A small amount of oxygen was found not to influence the addition of hydrogen bromide to crotonic acid either in the direction of addition, β -bromobutyric acid being the sole product, or in the rate of the reaction. The mixture of hydrogen bromide and oxygen, however, reacted with crotonic acid in carbon tetrachloride giving rise to three products, β -bromobutyric acid, crotonic acid dibromide, and α -hydroxy- β -bromobutyric acid. It was therefore concluded that, in the addition of hydrogen bromide to crotonic acid in the presence of oxygen, the oxygen participates in the reaction, as is the case with ordinary ethylenic compounds, producing bromine atoms from hydrogen bromide, and then the bromine atoms attach themselves to the β -carbon atom of crotonic acid to yield a free radical, $\text{CH}_3\text{CHBr}\dot{\text{C}}\text{HCOOH}$. The bromo radical gives rise to α -hydroxy- β -bromobutyric acid by a ready reaction, in contrast to radicals from the common ethylenic compounds, with oxygen rather than with hydrogen bromide. If the free radical had abstracted a hydrogen atom from a molecule of hydrogen bromide to yield β -bromobutyric acid and a bromine atom, the usual chain reaction of the abnormal addition would have taken place, and the addition to crotonic acid would have proceeded more rapidly in the presence of oxygen than in its absence. The experimental identification of the β -carbon atom of crotonic acid as the site of attack by bromine atoms supports the theory suggested by Mayo and Walling⁽²⁾ that of the alternative free radicals which can be produced by addition of a bromine atom the more stable is the one to be preferentially

(3) D. C. Grimshaw, J. B. Guy and J. C. Smith, *J. Chem. Soc.*, **1940**, 68; C. Walling, M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 2693.

(4) A. Michael and G. H. Shadinger, *J. Org. Chem.*, **4** (1939), 123.

(5) O. Simamura, this Bulletin, **17** (1942), 326.

produced. For the free radical $\text{CH}_3\text{CHBr}\dot{\text{C}}\text{HCOOH}$ is considered more stable than the isomeric radical $\text{CH}_3\dot{\text{C}}\text{HCHBrCOOH}$ by the resonance energy due to the conjugation of the odd electron at the α -carbon atom with the carboxyl group, whereas such an effect is absent in the later radical.

Experiments have now been extended to cinnamic acid. According to A. Michael⁽⁴⁾ cinnamic acid added hydrogen bromide to give only β -bromohydrocinnamic acid, but the result does not appear to be conclusive, as it does not seem that, in his investigation, due attention was paid to the various factors now accepted as influencing the course of the addition reaction.

Cinnamic acid was subjected to the action of hydrogen bromide in the presence of either benzoyl peroxide or catechol in benzene in a sealed tube kept at 60°C. The product in either case was found to be β -bromohydrocinnamic acid, and no appreciable difference in the reaction velocity was observed. On the other hand, when a mixture of hydrogen bromide and oxygen was passed into a suspension of cinnamic acid (10 g.) in benzene (70–80 c.c.) in the dark for 4 to 7 hours, the reaction vessel being cooled with ice water, a rather vigorous reaction took place with the evolution of heat. In the course of the reaction, water and a deposit, identified as α,β -dibromohydrocinnamic acid (m.p. 192°) as described in the experimental part, separated from the reaction mixture. On evaporation of the filtered benzene solution under reduced pressure at room temperature a residue was obtained, from which α,β -dibromohydrocinnamic acid and ω -bromoacetophenone were isolated. The ω -bromoacetophenone was certainly a scission product formed in the course of the reaction, and the other fragment, carbon dioxide, was found in the gas mixture escaping from the reaction vessel.

From these observations it is quite obvious that hydrogen bromide, oxygen, and cinnamic acid undergo a complicated reaction of just the same type as was already reported from this Laboratory.⁽⁶⁾ Thus the course of the reaction is considered to be as follows: The simultaneous action of hydrogen bromide and oxygen on cinnamic acid produces a free radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCHBrCOOH}$ and an unidentified substance (or substances) of peroxidic nature. α,β -Dibromohydrocinnamic acid is produced by the action of bromine liberated from hydrogen bromide by the action of the peroxidic substance on the free radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCHBrCOOH}$,⁽⁷⁾ a bromine atom being set free to add to cinnamic acid regenerating the same free

(6) Y. Urushibara and O. Simamura, this Bulletin, **14** (1939), 323; O. Simamura, *ibid.*, **15** (1940), 292 and reference 5.

(7) In an investigation of the addition of bromine to cinnamic acid in carbon tetrachloride, one of the present authors (O. Simamura, this Bulletin, **17** (1942), 280) has postulated that the addition takes place through a chain mechanism involving bromine atoms and the free radical which is formed by attachment of a bromine atom to the double bond of cinnamic acid. The structure of the radical was tentatively assumed to be $\text{C}_6\text{H}_5\text{CHBr}\dot{\text{C}}\text{HCOOH}$ on the basis of evidences available at that time. From the present results it is now concluded that, in that case also, the radical must have the structure $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCHBrCOOH}$.

radical. The acid may also be formed by the combined action of hydrogen bromide and oxygen on the free radical. The free radical is so stable that it cannot abstract a hydrogen atom from a molecule of hydrogen bromide to form α -bromohydrocinnamic acid and a bromine atom, which is subsequently to add to cinnamic acid forming the free radical and thus initiating the cyclic process of the chain addition reaction, but the free radical reacts at the β -carbon atom with oxygen, which has more or less unsaturated nature and is present comparatively in abundance in the reacting milieu, and ω -bromoacetophenone eventually is formed after decarboxylation.

There was no evidence to show the formation of the radical $\text{C}_6\text{H}_5\text{CHBr}\dot{\text{C}}\text{HCOOH}$, no compounds carrying a bromine atom on the carbon adjacent to the phenyl group, excepting α,β -dibromohydrocinnamic acid, having been obtained as reaction products. The isolation of α,β -dibromohydrocinnamic acid, which might be supposed to have been produced from the above radical and bromine, cannot be adduced as evidence in support of the formation of the radical in question, because, in view of the reactivity of such intermediate radicals in general, there is no reason why this radical should not react with oxygen as well, if not with hydrogen bromide, giving rise to products carrying a bromine atom on the carbon adjacent to the phenyl group.

The formation of the radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCHBrCOOH}$ in preference to the alternative radical $\text{C}_6\text{H}_5\text{CHBr}\dot{\text{C}}\text{HCOOH}$ is easily accounted for on the basis of considerations analogous to those advanced by Mayo and Walling by the reasonable assumption that the former will be more stable than the latter because of the greater resonance energy due to the conjugation of the free valency electron on the β -carbon atom with the phenyl group than that due to the conjugation of the free valency electron on the α -carbon atom with the carboxyl group.

It was argued previously⁽⁵⁾ that if cinnamic acid was to add hydrogen bromide to give only β -bromohydrocinnamic acid even under the conditions favourable to the abnormal addition, this might well be attributable to the circumstances that the theoretically more stable radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCHBrCOOH}$, owing to its relatively great stability, reacts with hydrogen bromide with more difficulty than does the isomeric β -bromohydrocinnamic radical. However, the possibility of the formation of β -bromohydrocinnamic acid through the chain mechanism under usual oxygenic conditions can now be ruled out, for, in the first place, the reaction under such conditions did not appear to be faster than that in the presence of catechol, and secondly, in the reaction with a large amount of oxygen it was demonstrated that only the α -carbon atom of cinnamic acid is attacked by bromine atoms.

β -Bromohydrocinnamic acid is formed only by the normal addition of hydrogen bromide, and that even in the presence of benzoyl peroxide. As the normal reaction is a slow one, it could not compete to advantage

with the abnormal addition which should produce α -bromohydrocinnamic acid through the chain mechanism, if the radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCHBrCOOH}$ were active enough to react readily with hydrogen bromide to initiate the chain.

In view of the relative stability of the radical postulated above it is supposed that the dimerization of it may have taken place. Although no compound resulting from the dimerization was found, this will not detract from the possibility of the operation of the reaction mechanism involving the free radical, inasmuch as the dimerization of usually scarce radicals would take place only under exceptionally favourable conditions provided by a very inert medium containing no reactive substances, such as oxygen.

Experimental Part

Materials. Hydrogen bromide was generated by dropping bromine on hot tetralin, and passed through a bottle containing cold tetralin, and then through a tube containing glass wool sprinkled with phosphorus pentoxide. For experiments in sealed tubes the hydrogen bromide was collected in a tube cooled with liquid air. Then the condensed hydrogen bromide was subjected to repeated fusion and solidification in vacuum to eliminate traces of incondensable gases. Cinnamic acid was synthesized from benzaldehyde, acetic anhydride, and anhydrous sodium acetate, and recrystallized from alcohol several times. It melted at $132.0\text{--}2.5^\circ\text{C}$. Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and distilled. Benzene was shaken with concentrated sulphuric acid several times until the sulphuric acid layer was colourless, dried with calcium chloride, and distilled over sodium.

The Addition of Hydrogen Bromide to Cinnamic Acid in Benzene in a Sealed Tube. In a glass tube with a capacity of 70 c.c. cinnamic acid (4 g.) and benzene (15 c.c.) together with benzoyl peroxide (0.2 g.) or catechol (0.1 g.) were placed, and the tube was connected to the vacuum line. In order to remove oxygen the contents of the tube were solidified by cooling with liquid air, and the tube was evacuated with a mercury diffusion pump. The contents were then melted, again solidified, and the tube was evacuated to 0.0005 mm. of mercury. The procedure was repeated three times. Then a measured quantity of hydrogen bromide (1.5 c.c. at the temperature of solid carbon dioxide and ether) was condensed on the top of the solidified mixture, and the tube was sealed off. The tube was kept at about 60° in a hot water bath in the day-time. After five days the reaction tube was opened, and the benzene solution was filtered from a precipitate. The solid product (m.p. 134° , 4.9 g. in the experiment with catechol) which was already nearly pure was recrystallized from carbon disulphide and identified as β -bromohydrocinnamic acid. In the experiment with benzoyl peroxide, in addition to the above product (4.1 g.), on evaporation of the filtered benzene solution a solid residue (1.2 g., m.p. $98\text{--}123^\circ$) was obtained, from which a further crop of β -bromo-

hydrocinnamic acid was separated.

The Action of the Mixture of Hydrogen Bromide and Oxygen on Cinnamic Acid in the Dark. The essential part of the experiments has already been described above. After the reaction was complete, the deposit (α , β -dibromohydrocinnamic acid, m.p. 192°) was separated from the solution, weighed (10.4 to 11.4 g.) and analyzed for bromine (found: Br, 48.2%). On recrystallization from carbon disulphide the bromine content was improved to 51.2% (calculated for $C_9H_8O_2Br_2$: Br, 51.9%). By removing the solvent from the solution under diminished pressure a residue (2.8 to 3 g.) consisting of a yellow oil and a small amount of a crystalline substance identified as α , β -dibromohydrocinnamic acid were obtained. The oil was dissolved in ether, dried with anhydrous sodium sulphate, and distilled under reduced pressure. The lachrymatory distillate, which passed over at $78-82^\circ$ under 0.75 mm., was analyzed for bromine (found: Br, 39.2%). By cooling this distillate in an ice-box plate crystals were obtained, which after recrystallization from alcohol melted at $50-51^\circ$ (found: Br, 40.2%; calculated for C_9H_7OBr : Br, 40.2%). The melting point of the substance was not depressed on admixture with an authentic specimen of ω -bromoacetophenone.

The gas issuing from the reaction vessel was passed through a bottle containing water and then through one containing an aqueous barium hydroxide solution. The precipitated barium carbonate was dried and weighed. The amount of carbon dioxide evolved was estimated at 0.089 to 0.209 mole per mole of the cinnamic acid used.

The product of addition of hydrogen bromide to cinnamic acid is β -bromohydrocinnamic acid either under the antioxidant condition or in the presence of benzoyl peroxide.

Summary

The action of the mixture of hydrogen bromide and oxygen on cinnamic acid in carbon tetrachloride produces ω -bromoacetophenone together with α , β -dibromohydrocinnamic acid. It is concluded that the free radical $C_6H_5\dot{C}HCHBrCOOH$ is formed in the intermediate stage in accord with the expectation from theoretical considerations concerning the stability of radicals. The radical, owing to its stability, does not react with hydrogen bromide to give α -bromohydrocinnamic acid, but reacts, on one hand, with oxygen ultimately to give ω -bromoacetophenone after disrapture of carbon dioxide and, on the other hand, with bromine or hydrogen bromide, as detailed in the text, to give α , β -dibromohydrocinnamic acid.

The authors express their sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work.

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New Diffusion Pump Oil—Higher Monoalkyl-naphthalenes.

By Tutomu KUWATA, Sin-ichi TOMIYAMA and Masayasu TAKAO.

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Introduction. C. R. Burch⁽¹⁾ who first used organic liquid, in place of mercury, for diffusion pump medium obtained the vacuum of 10^{-6} mm-Hg, using a special fraction of lubricating oil of paraffin series and no cooling trap. Hickman and his collaborators⁽²⁾ reported later that esters of phthalic acid or sebacic acid have suitable properties as diffusion pump oil and obtained the high vacuum of 1×10^{-7} mm-Hg by using octyl phthalate (Octol) and octyl sebacate (Octoils). Sagane, Haruta and others⁽³⁾ have tested a synthetic oil, "Kao" oil, which was prepared from olefine hydrocarbons derived from higher fatty acids using aluminium chloride as a polymerization catalyst and showed the oil to be as good as Apiezon B or Octoil S in regard to vacuum and stability when used as diffusion pump oil.

One of the present authors (T. Kuwata) has found a new synthetic method of preparing higher alkyl-naphthalenes from higher alcohols and naphthalene by the dehydrating and alkylating action of Japanese acid clay.⁽⁴⁾ The process is relatively simple and gives good yield of condensate. For example, when 250 g. of cetanol and 100 g. of naphthalene were heated in the presence of 75 g. of activated Japanese acid clay, elimination of water began at the neighbourhood of 190°C . The heating was continued at $190\text{--}210^{\circ}\text{C}$. until the evolution of water vapour ceased, the catalyst was filtered off, and then the resultant oil was distilled under reduced pressure, obtaining 260 g. of the product of which ca. 45% were monoalkyl-naphthalene and 35% were dialkyl-naphthalene with small amount of tri-derivative. The saturated paraffin hydrocarbon containing no naphthalene ring amounted to ca. 10% of the product.

The present report concerns the properties of some of higher alkyl-naphthalenes, such as monododecyl, monotetradecyl, monohexadecyl and monooctadecyl-naphthalenes obtained by the process above mentioned.

Preparation and Properties of Monoalkyl-naphthalenes. 20 kg. of crude higher alcohols (Sp. v. 9.6, Ac. v. 212.5), which were prepared by the catalytic reduction of coconut oil, were rectified under reduced pressure using a column 1 m. long filled with Stedman's wire gauze corn, and pure dodecyl alcohol was obtained. The higher fraction was changed into acetic ester, and repeating its fractional distillation, pure acetic ester of tetradecyl alcohol was obtained. Pure hexadecyl and octadecyl

(1) C. R. Burch, *Proc. Roy. Soc., A*, **23** (1929), 271.

(2) Hickman, *Frank. Inst.*, **321** (1946), 381.

(3) Sagane etc., *Kagaku*, **14** (1944), 315.

(4) T. Kuwata *J. Chem. Soc., Japan, Ind. Section*, **52** (1949), 146.

alcohols were prepared by the repeated fractionation of 3 kg. of crude cetanol (Sp. v. 0.5, Ac. v. 186).

The higher alcohols thus obtained had the following properties.

Table 1. Properties of Pure Higher Alcohols and their Acetic Esters.

		Dodecyl alcohol	Tetradecyl alcohol	Hexadecyl alcohol	Octadecyl alcohol
Acetate	Boiling point (°C/mm.)	—	129-131/1	147-150/1	166-168/1
	Sp. v. obs.	—	220.1	199.5	178.8
	calc.	—	219.0	199.0	179.6
	M. p. obs.	—	—	21.5-22.0	30.0-30.5
	lit.	—	—	22.7	31
Free alcohol	B. p. (°C/mm.)	110-112/1	125-126/1	142-144/1	159-161/1
	Ac. v. obs.	241.9	219.8	199.2	179.1
	cal.	243.8	219.0	199.0	179.6
	M. p. obs.	24.5-25.0	37.0-35.5	48.5-49.5	58-59
	lit.	24	38	50	59

The dehydrating condensation of these alcohols with naphthalene was carried out at 200°C. for 60 minutes. The resultant product was purified by the fractional distillation under the pressure of 1×10^{-2} mm-Hg and then 5×10^{-3} mm-Hg. The properties of monoalkyl-naphthalenes thus obtained were shown in Table 2.

Table 2. Properties of Higher Monoalkyl-naphthalenes.

		Dodecyl- naphthalene	Tetradecyl- naphthalene	Hexadecyl- naphthalene	Octadecyl- naphthalene
Boiling pt. (1 mm-Hg)		180-182°C.	198-200°C.	212-214°C.	226-228°C.
Specific gravity (30°/4°)		0.9107	0.9055	0.8991	0.8942
Refractive index (30°/D)		1.5262	1.5240	1.5219	1.5192
Specific refraction (n_D^{30})		0.3371	0.3379	0.3392	0.3395
Mol refraction	obs.	99.61	108.80	118.48	127.73
	calc.	99.06	106.30	115.43	123.67
Mol. weight	obs.*	295	322	349	376
	calc.	296	324	352	379
Solidifying pt.		-42°C.	—	—	-16°C.
Viscosity	210°F	37.0	39.4	41.7	44.6
	(S. U. S.) 100°F	90.0	113.5	140.5	173.9
Viscosity index		6.16	50.5	74.1	97.6
Elementary analysis	C %	obs.	88.82	89.42	88.36
		calc.	89.11	88.82	88.56
	H %	obs.	10.87	11.46	11.47
		calc.	10.88	11.18	11.44

* Cryoscopic method.

The values cited in Table 2. differ from those reported by Mikeska and his collaborators,⁽⁵⁾ i. e. n-octadecyl-naphthalene of Mikeska melted at 51–52°C. and had viscosity index of 144. The constitution of monoalkyl-naphthalenes of the present authors has not yet been confirmed, but they may be assumed to be 2-naphthyl alkanes.

Vacuum Test of Monoalkyl-Naphthalenes. The vacuum test of the oil was carried out by the diffusion oil pump of Hickman type. The pump was charged with the testing oil and put on action for 5–6 hours, and then heating was controlled at the intervals of 30 minutes so as to obtain the optimum vacuum which was measured by ionization gauge. The data are shown in Table 3.

In order to test the oxidation stability of the oils, the air was introduced into the acting pump, continuing the heating until the pressure dropped to atmospheric pressure. After the lapse of 2 minutes, the pump was put again on action, and the restoration time and maximum attainability of vacuum were observed. On repeating the same process for 4 times, the "Kao" oil showed the evident deterioration, while alkyl-naphthalenes rather shortened the restoration time and increased the maximum vacuum.

Table 3. The Highest Attainability of Vacuum.

Monododecyl-naphthalene	2.1×10^{-6} mm-Hg
Monotetradecyl-naphthalene	5.2×10^{-6} „
Monohexadecyl-naphthalene	4.5×10^{-6} „
Monooctadecyl-naphthalene	1.2×10^{-5} „
"Kao" oil	3.0×10^{-6} „

Among the alkyl-naphthalenes used in the present studies, monododecyl-naphthalene was the most excellent as diffusion pump oil in regard to the action of the pump at relatively low temperature and the attainability of high vacuum.

Summary. Some monoalkyl-naphthalenes were prepared by the condensation of naphthalene and respective alcohols using activated Japanese acid clay as a condensing catalyst. The constitution of the alkyl-naphthalenes was assumed to be 2-naphthyl alkanes. The alkyl-naphthalenes were shown to be usable as good diffusion pump oil. The oils were very resisting for oxidation.

The authors wish to express their best thanks to Dr. Imachi of Horikawa Factory of Tokyo-Shibaura Electric Co. for his kind and earnest aid in the vacuum tests.

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(5) Mikeska etc., *Ind. Eng. Chem.*, **29** (1937), 970.

The Scission Reactions of the Oxido Ring in Cholesterol Oxides.⁽¹⁾

By Yoshiyuki URUSHIBARA and Misao CHUMAN.

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The scission reactions of the oxido ring in α - and β -cholesterol oxides have been studied in this laboratory since one of the authors⁽²⁾ derived the configurations of these stereoisomeric oxide compounds and related diols from that of the so-called α -cholestanetriol which had been determined to be cholestanetriol-(3 β ,5 α ,6 β) (III) by Ellis and Petrow.⁽³⁾ A β -oxido structure (II) of β -cholesterol oxide was concluded from the change of the α -cholestanetriol (III) to this oxide through a 5-chlorodi-ol-(3 β ,6 β) (IV), and consequently an α -oxido configuration (I) was assigned to α -cholesterol oxide. Further, the Δ^4 -cholestenediol-(3,6) melting at 257–258° was found to be Δ^4 -cholestenediol-(3 β ,6 β) (V), because it is obtainable from the triol (III) by a Darzens dehydration of its diacetate followed by saponification, and the 6-isomeride melting at 178–179° proved to be Δ^4 -cholestenediol-(3 β ,6 α) (VI). The cholestanediol-(3,6) melting at 194–195° was given a configuration of cholestanediol-(3 β ,6 β) (VII), because it is obtained by a catalytic reduction of the higher melting unsaturated diol (V), and hence its 6-isomeride melting at 216° should be cholestanediol-(3 β ,6 α) (VIII).

Reduction of Cholesterol Oxides with Sodium and Amyl Alcohol.⁽⁴⁾

As described in details elsewhere,⁽⁴⁾ on reduction with sodium and amyl alcohol α -cholesterol oxide (I) gave cholestanediol-(3 β ,6 α) (VIII), while pure β -cholesterol oxide (II), prepared from α -cholestanetriol (III) through the chlorohydrin (IV), was reduced to the same cholestanediol-(3 β ,6 α) (VIII). The formation of cholestanediol-(3 β ,6 α) from the α -oxide appeared quite natural, but an explanation was required for the formation of a cholestane derivative with a 6 α -hydroxyl group from the β -oxide (II). An inversion of the β -oxide to the α -isomeride prior to reduction under the conditions of the reaction, especially by the action of sodium amylate, was first suspected but disproved by experiments: When the β -oxide was heated with sodium amylate it was reduced to cholestanediol-(3 β ,6 α) while the α -oxide was not reduced when treated similarly, and the β -oxide was not changed when heated with sodium ethylate. Therefore, it is very probable that the reduction of the β -oxide to cholestanediol-(3 β ,6 α) did not go through the α -oxide.

(1) Abstracts from the doctor theses by M. Chuman. For originals consult the footnotes under respective subtitles.

(2) Y. Urushibara, this Bulletin, **16** (1941), 182.

(3) B. Ellis and V. A. Petrow, *J. Chem. Soc.*, **1939**, 1078.

(4) M. Chuman, *J. Chem. Soc. Japan*, **64** (1943), 1369.

When the 3,6-diol was formed from the β -oxide by reduction, the oxido ring was opened between carbon atom 5 and the oxido oxygen atom. Then the formation of a cholestane derivative from the β -oxide can be understood on the assumption of a Walden inversion at carbon atom 5; but a 6 β -hydroxyl group should be produced from the oxygen atom in β -configuration. Consequently, it must be assumed that the 6 α -hydroxyl group in the product was formed through an inversion from the primarily introduced 6 β -hydroxyl group. Experiments showed it was really the case: When cholestanediol-(3 β ,6 β) (VII), prepared from 6-keto-cholestanol by catalytic reduction,⁽⁵⁾ was heated with sodium amylate, it was transformed into cholestanediol-(3 β ,6 α) (VIII). Such an inversion of a newly formed hydroxyl group would have been possible also in the reduction of α -cholesterol oxide, if the hydroxyl group had had an unstable configuration; but the 6 α -hydroxyl group formed primarily by the scission of the α -oxido ring was stable to sodium amylate and remained without inversion. The 3 β -hydroxyl group in the reduction product is considered stable to alcoholates as so is that in cholestanol. A problem may arise rather from the fact that the oxido ring in α -cholesterol oxide is opened between carbon atom 5 and the oxygen atom by the action of sodium and amyl alcohol, because it is the only exceptional behaviour of the α -oxide ever experienced in its scission reactions.

Catalytic Reduction of Cholesterol Oxides.⁽⁶⁾

Earlier experiments on catalytic reduction showed that α -cholesterol oxide is difficultly reduced while β -cholesterol oxide is reduced too far to cholestane and cholestanol. Even such undesired over-reduction indicated that the β -oxide is not reduced to a coprostane derivative which might be expected from the configuration given to it. Catalytic reduction of the acetates with platinum oxide in glacial acetic acid was finally successful both in reducing the α -oxide and in obtaining from the β -oxide a product retaining the oxygen atom of the oxido ring. Thus, β -cholesterol oxide acetate (II') gave cholestanediol-(3 β ,6 β) 3-acetate (VII'), m.p. 155–156°, along with cholestane and cholestanol acetate. Hydrolysis gave free cholestanediol-(3 β ,6 β) (VII) identical with the specimen prepared from 6-keto-cholestanol by catalytic reduction.

A similar reduction of α -cholesterol oxide acetate (I') yielded a product melting at 178–179° and sparingly soluble in alcohol. It remained unchanged on boiling with acetic anhydride, thus showing the newly formed hydroxyl group, if any, was tertiary. Saponification with alcoholic potash gave a substance melting at 220–221° and difficultly soluble in ether. Analysis gave numbers calculated for a cholestanediol. The diol was oxidized with chromic acid to a substance melting at 231–232°, and dehydration of the latter produced the known Δ^4 -cholestenone (XI). Hence, the new diol is a 3,5-diol, and the oxido ring was opened by reduc-

(5) R. E. Marker and J. Krueger, *J. Am. Chem. Soc.*, **62** (1940), 79.

(6) M. Chuman, *J. Chem. Soc. Japan*, **64** (1943), 1486.

tion between carbon atom 6 and the oxygen atom; and thus the 5-hydroxyl group must necessarily possess an α -configuration. Consequently, the diol is cholestanediol-(3 β ,5 α) (IX), and the substance, m.p. 178–179°, obtained primarily by the reduction of α -cholesterol oxide acetate is its 3-monoacetate (IX'). The product, m.p. 231–232°, from the oxidation of the free diol which gave Δ^4 -cholestenone by dehydration is 5 α -hydroxy-cholestanone-(3) (X). Designation " α " after position number "5" may be omitted in the names of the cholestane derivatives, because it is implicitly expressed by term "cholestane".

The course of reactions starting from a 5,6 α -oxido steroid and leading to an α,β -unsaturated 3-keto-steroid was successfully applied to the synthesis of testosterone⁽⁷⁾ and progesterone.⁽⁸⁾

Recently the authors became aware of the publication of similar works on catalytic reduction of cholesterol oxides by Stavely⁽⁹⁾ and by Plattner and others,⁽¹⁰⁾ although the original papers are not available here. The former, reducing α -cholesterol oxide with a palladium catalyst and obtaining cholestanediol-(3,5) monoacetate after acetylation, seems to have suggested that when an ethylene oxide ring is opened by hydrogenation the hydroxyl group formed will be attached to the carbon atom carrying the smaller number of hydrogen atoms. The latter reduced both α - and β -cholesterol oxide acetates with the same catalyst as used by the present authors and obtained similar results. The melting points of their products as quoted in the *Chemical Abstracts*, however, do not show any good coincidence with those obtained for the corresponding substances by the present authors, some being higher and others lower. The discrepancies in the melting points may be due to either different purities or otherwise possible polymorphism of crystals.

Action of Aluminium Amalgam and of Aluminium Isopropylate and Isopropyl Alcohol on Cholesterol Oxides.⁽¹¹⁾

Attempted reduction with aluminium amalgam and with aluminium isopropylate and isopropyl alcohol yielded none of reduced compounds. α -Cholesterol oxide was attacked by neither of the reagents. β -Cholesterol oxide, on the other hand, was hydrated to cholestanetriol-(3 β ,5 α ,6 β) (III) on treatment with the former reagent in hydrous alcohol, while it was isomerized to Δ^4 -cholestenediol-(3 β ,6 β) (V) by the latter reagent.

Hydration of Cholesterol Oxides.⁽¹²⁾

α -Cholesterol oxide is long known to give α -cholestanetriol, namely, cholestanetriol-(3 β ,5 α ,6 β) (III), when heated with water in a sealed tube, while the hydration reaction of β -cholesterol oxide had not yet been studied

(7) Y. Urushibara and M. Chuman, this Bulletin, **22** (1949), 1.

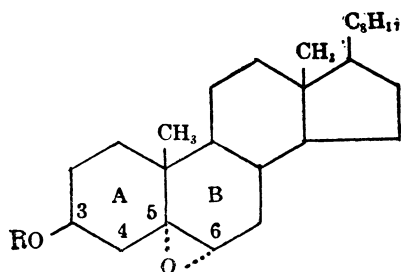
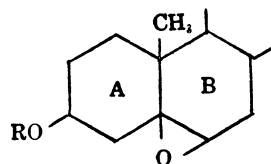
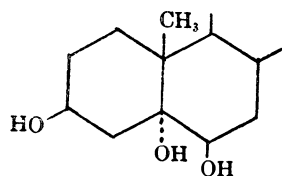
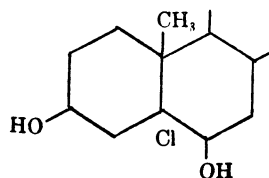
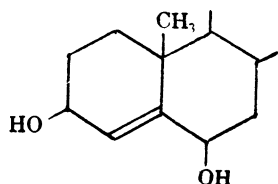
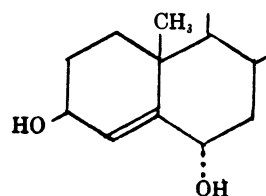
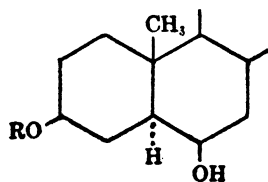
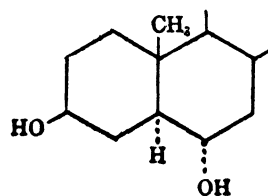
(8) Y. Urushibara, M. Chuman, and S. Wada, this Bulletin, in press.

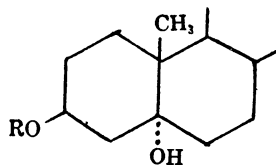
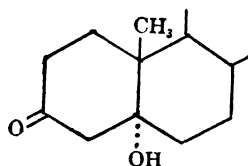
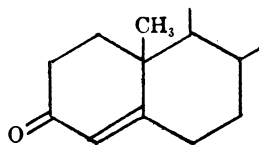
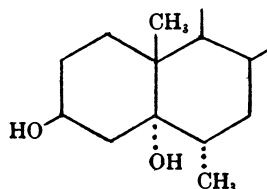
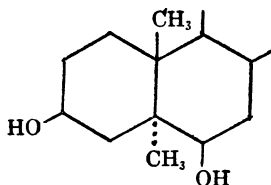
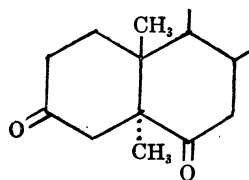
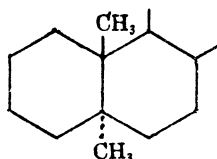
(9) H. E. Stavely, *Chemical Abstracts*, **37** (1943), 652.

(10) Pl. Plattner, Th. Petrzilka, and W. Lang, *Chemical Abstracts*, **38** (1944), 6295.

(11) M. Chuman, *J. Chem. Soc. Japan*, in press.

(12) M. Chuman, *J. Chem. Soc. Japan*, in press.

(I) $R = H$: α -Cholesterol oxide.(I') $R = CH_3CO$: Acetate of I(II) $R = H$: β -Cholesterol oxide(II') $R = CH_3CO$: Acetate of II(III) α -Cholestanetriol,
Cholestanetriol-(3β , 5α , 6β)(IV) 5-Chloro-cholestanediol-(3β , 6β)(V) Δ^4 -Cholestenediol-(3β , 6β)(VI) Δ^4 -Cholestenediol-(3β , 6α)(VII) $R = H$: Cholestanediol-(3β , 6β)(VII') $R = CH_3CO$: 3-Acetate of VII(VIII) Cholestanediol-(3β , 6α)

(IX) R = H: Cholestanediol-(3 β , 5 α)(IX') R = CH₃CO: 3-Acetate of IX(X) 5 α -Hydroxy-cholestanone-(3)(XI) Δ^4 -Cholestenone(XII) 6 α -Methyl-cholestanediol-(3 β , 5 α)(XIII) 5 α -Methyl-cholestanediol-(3 β , 6 β)(XIV) 5 α -Methyl-cholestanedione-(3, 6)(XV) 5 α -Methyl-cholestane

with a pure specimen. The hydration reactions of these isomeric oxides were compared under various conditions with the following results:

The β -oxide did not react with water at such temperatures (120°, 14 hours, and 160°, 10 hours) as were high enough to cause the hydration of the α -oxide, but gave the same α -cholestanetriol (III) at a much higher temperature (over 200°, 10 hours). With slightly acidic water (one drop of 10% sulfuric acid to 1 c.c.) both oxides were easily hydrated to the triol (at 120°, 10 hours). With slightly alkaline water (one drop of 5% caustic potash to 1 c.c.), however, neither reacted (at 120°, 10 hours). With a stronger aqueous alkali (2% potassium hydroxide solution) and at a higher temperature (160–170°, 10 hours) the α -oxide was partly

(20%) hydrated, while the β -oxide still remained unchanged.

Thus the isomeric cholesterol oxides manifested a very striking difference in easiness of hydration, and, as ethylene oxide derivatives are generally so, proved to be weak to acid and stable in alkaline media, much more stable than in neutral water.

The formation of cholestanetriol-($3\beta,5\alpha,6\beta$) (III) from both α - and β -cholesterol oxides indicates that the oxido ring is opened by hydration between carbon atom 6 and the oxygen atom in the α -oxide and between carbon atom 5 and the oxygen atom in the β -oxide, and the carbon atom cut off from the oxygen atom undergoes an inversion in each case to give the same cholestanetriol.

Action of Grignard's Reagent on Cholesterol Oxides.⁽¹³⁾

Ushakov and Madaeva⁽¹⁴⁾ obtained a 6-methyl-cholestanediol-($3,5$), m.p. $181-181.5^\circ$, from Grignard's reaction of α -cholesterol oxide. The present authors obtained an isomeric methyl-diol, m.p. $195-196^\circ$, by the action of methyl-magnesium iodide on β -cholesterol oxide, and demonstrated that the new methyl-diol was a 5-methyl-diol-($3,6$) by obtaining a diacetate, m.p. $132-133^\circ$, by the action of acetic anhydride and a diketone, m.p. $194-195^\circ$, by the oxidation with chromic acid. The dibenzoate, m.p. $152-153^\circ$, of the methyl-diol was also prepared. The diketone yielded the corresponding hydrocarbon, m.p. $94-95^\circ$, by Clemmensen reduction.

On the assumption that no inversion took place at carbon atom 6 obtaining a methyl group from Grignard's reagent a configuration of 6α -methyl-cholestanediol-($3\beta,5\alpha$) (XII) was given to the methyl-diol of Ushakov and Madaeva. On the other hand, a structure of 5α -methyl-cholestanediol-($3\beta,6\beta$) (XIII) was deduced for the 5-methyl-diol-($3,6$), because β -cholesterol oxide gives cholestane derivatives in all other scission reactions. Consequently, the diketone from the 5-methyl-diol is 5α -methyl-cholestanedione-($3,6$) (XIV) and the hydrocarbon from the diketone 5α -methyl-cholestane (XV).

The chlorohydrin, 5-chloro-cholestanediol-($3\beta,6\beta$) (IV), obtained by the action of hydrogen chloride on cholestanetriol-($3\beta,5\alpha,6\beta$) (III), yielded the same 5-methyl-cholestanediol-($3\beta,6\beta$) (XIII) on treatment with methyl-magnesium iodide.

In a separate paper a stereochemical interpretation of the scission reactions of cholesterol oxides will be presented, and in another it will be shown that the α - and β -oxides of Δ^5 -cholestenone correspond respectively to β - and α -cholesterol oxides in the behaviours in scission reactions.

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(13) M. Chuman, *J. Chem. Soc. Japan*, in press.

(14) *Brit. Chem. Abst.*, **1939**, A (II), 367.

perature. In general, especially in a non-uniform flow θ is a function of θ, φ which are respectively the polar coordinates of one molecule taking the other as an origin. The directional difference of θ may be small in comparison with the magnitude of θ and when we put the mean value of θ as equal to T , we may get:

$$\theta = T + \Delta\theta(\theta, \varphi) \quad \langle \Delta\theta(\theta, \varphi) \rangle_{AV} = 0 \quad (1)$$

where $\Delta\theta$ is a function of θ, φ and the average is taken over all possible directions. In this case f can be expressed as follows:

$$f(R, \theta) = f(R, T) + \Delta\theta \partial f / \partial T \quad (2)$$

When the non-uniformity of a flow is expressed by a single flow gradient du/dz , where u is a flow velocity on x -direction, and the other flow gradients are zero, the consideration on the space symmetry deduces that at $\theta = 0$, $\Delta\theta = 0$, and variation of the directional variation of $\Delta\theta$ is a periodic function of θ and φ having periods π and 2π respectively. Then we may write $\Delta\theta$ in the following simple expression;

$$\Delta\theta = \alpha \sin 2\theta \sin(\varphi + \delta) \quad (3)$$

where α is a constant depending on du/dz and δ is a constant which will be determined in the next section.

Only the forces f between the nearest neighbours are taken into consideration, so we can easily obtain the shearing force in a liquid. If we denote by F_x the x -component of a shearing force per unit area of x, y -plane at the origin of coordinates, we may obtain F_x as a sum of x -component of the forces which act between the molecules on one side of x, y -plane (e.g. $z > 0$) and the molecules on the other side ($z < 0$). Then we may write:

$$F_x = \int_0^R \int_0^{2\pi} \int_0^{\cos^{-1}(z/R)} f(R, \theta) \sin \theta \cos \varphi (Z_m/4\pi) \sin \theta d\theta d\varphi \rho dz \quad (4)$$

where ρ is the particle density of molecules in a liquid. $f(R, \theta) \sin \theta \cos \varphi$ is x -component of a force f between a molecular pair having the distance R and direction θ, φ . $(Z_m/4\pi) \sin \theta d\theta d\varphi \rho dz$ is the number of molecular pairs which have one of pair having a coordinate z between z and $z+dz$ and the other one having the direction θ, φ respectively in the small region $(\theta, \theta+d\theta)$ and $(\varphi, \varphi+d\varphi)$. The value of θ is restricted within $0 \leq \theta < \cos^{-1}(z/R)$ by the condition that one has a coordinate $z \leq 0$ and the other $z > 0$.

The pressure P in a liquid may be considered as a z -component of a force per unit area of x, y -plane acting on one side of the plane by molecules in the other side of the plane. Then in the same manner as

above we may obtain the formula for P , but this time we have to take into consideration the kinetic pressure NkT/V .

$$P = NkT/V + \int_0^R \int_0^{2\pi} \int_0^{\cos^{-1}(Z/R)} f(R, \theta) \cos \theta (Z_m/4\pi) \sin \theta d\theta d\varphi \rho dz$$

Where V is molar volume; N , Avogadro's number, and $f \cos \theta$ is z -component of a force f . The same result may be obtained by the use of the virial theorem. This integral is easily performed with the aid of equations (2) and (3). It is obvious that the result obtained is independent of u , i. e. of gradient of flow.

$$P = NkT/V + (1/6) Z_m \rho R f(R, T) \quad (5)$$

In the actual case, distance R and number Z_m of the nearest neighbour depend on V and T in a complicated manner, but the approximation that R and Z_m explicitly depend only on V may be allowed in a simple liquid model. By this assumption we can obtain $\partial f/\partial T$ in equation (2) by differentiation (5) with respect to T .

$$\partial f/\partial T = (6/Z_m \rho R) [(\partial P/\partial T)_v - Nk/V] \quad (6)$$

The integration of equation (4) is performed by equations (2) and (3), and referring to equation (6) the next result is obtained:

$$F_x = (2\alpha/5) [(\partial P/\partial T)_v - Nk/V] \quad (7)$$

where a constant δ is substituted by $\pi/2$ as we shall see in the next section.

The Gradient of the Flow Velocity. The molecular motion in a liquid may be considered as jumps of a molecule from one equilibrium point to another. The simplest assumption we can make is that the distance of a jump is equal to R , since a molecule jumps to any one of its nearest neighbour sites. When one molecule changes its site, it is naturally expected that some of its neighbouring molecules may change their sites at almost the same time, therefore we cannot make clear the idea of the equilibrium site of a molecule. On the contrary, the change in direction θ, φ or distance R of two molecules is the evidence of a jump of a molecule.

We suppose that a molecule A is situated at the origin and the polar coordinates of molecule B are at first R, θ, φ respectively. Now we consider a jump of molecule B which changes θ, φ to θ', φ' but keeps R constant. Molecules which hinder this kind of transition are A and some of the other nearest neighbours of B molecule. These other molecules besides A, might jump in the process of transition of B molecule. A detailed discussion about the motion of these molecules is very dif-

ficult. But we can say that the potential barrier formed by these molecules is fixed to the molecule A, i. e. to the origin of the coordinates. The probability that the molecule B passes over this potential barrier will be given by $\lambda \exp(-\omega/k\theta)$ where ω is the height of this barrier and θ is a quantity having a dimension of temperature which represents the thermal motion of B with respect to A as mentioned in the preceding section. A constant λ may be determined as follows. The consideration on the uniform state i. e. $\theta = T$, may be allowed now. In this case the probability of jumps of a molecule may be proportional to the number of available sites around this molecule. Therefore the probability of jumps of a molecule in any direction may be proportional to the number of the nearest neighbour sites Z_g , but the probability of jumps mentioned above i. e. the jumps of B to the nearest neighbour sites of A may be proportional to the number of the nearest neighbour sites common to A and B. If we denote by Z_c this number of sites, we may write these proportional relations in the following manner.

$$\nu \exp(-\omega/kT) / \lambda \exp(-\omega/kT) = Z_g/Z_c$$

Therefore $\lambda = \nu Z_c/Z_g$

The numerator of the left side of the above equation implies a probability of jumps in any direction as given by Simha.⁽²⁾ Now we can obtain a number of jumps of B per unit time which changes θ, φ to θ', φ' but keeps R , the distance from A, constant.

$$(\nu Z_c/Z_g) \exp(-\omega/k\theta) \quad (8)$$

Suppose there is a spherical shell with a radius R around one molecule in a liquid. We consider the conservation of the number of molecules on the small area $R^2 dw$ on this sphere, which is intercepted by the small solid angle dw drawn at the center and directed to θ_1, φ_1 . The molecules on the area $R^2 dw$ jump away from this area by two processes, one changing only the coordinates θ_1, φ_1 and keeping R constant, the other changing R . At first we consider the latter process and its reverse i. e. jumping-in-process. These processes are the change in position of the molecules taking place on and outside of the sphere, therefore the net rate of increase of molecules on the area $R^2 dw$ in these processes may be written as follows:

$$\rho(du/dz) R \cos \theta_1 \sin \theta_1 \cos \varphi_1 R^2 dw \quad (9)$$

where $(du/dz) R \cos \theta_1$ is a flow velocity in the x -direction in the small area $R^2 dw$, and $\sin \theta_1 \cos \varphi_1 R^2 dw$ is an area projected to the y, z -plane. On the other hand jumps of the former case and its reverse process are

(2) R. Simha, *J. Chem. Phys.*, 7 (1938), 202.

changes of molecules on the same sphere. The number of molecules jumping away from the area $R^2 dw$ per unit time by the change of θ_1 , φ_1 is expressed in a product of $\nu(Z_c/Z_g) \exp(-\omega/k\theta_1)$ and $(Z_m/4\pi) dw$, which is equal to the number of molecules in this area, where θ_1 means $\theta(\theta_1, \varphi_1)$. The reverse processes bring molecules to the area $R^2 dw$ from the small circle k on the spherical shell around A. The center and the radius of this circle are respectively the small area $R^2 dw$ and R . The number of molecules brought in by this process per unit time may be given by the product of the averaged value of (8) around the circle k and $(Z_m/4\pi) dw$. Therefore the net rate of increase per unit time in these two processes are

$$\nu(Z_c/Z_g) [\langle \exp(-\omega/k\theta) \rangle_{AV} - \exp(-\omega/k\theta_1)] (Z_m/4\pi) dw \quad (10)$$

The sum of the expressions (9) and (10) is the total increase of molecules in the small area $R^2 dw$ by any sort of jumps, therefore this must be zero and we obtain

$$\cos \theta_1 \sin \theta_1 \cos \varphi_1 (du/dz) = (\nu Z_m Z_c / 4\pi \rho R Z_g) (\exp(-\omega/k\theta_1) - \langle \exp(-\omega/k\theta) \rangle_{AV}) \quad (11)$$

Then, using equations (1) and (3) we can write

$$\exp(-\omega/k\theta_1) - \langle \exp(-\omega/k\theta) \rangle_{AV} = (\alpha\omega/kT^2) [\sin 2\theta_1 \sin(\varphi_1 + \delta) - \langle \sin 2\theta \sin(\varphi + \delta) \rangle_{AV}] \exp(-\omega/kT) \quad (12)$$

When θ, φ are the coordinates of a point on the circle k and φ' is a parameter illustrated by Fig. 1. The calculation of the last term is performed by spherical trigonometry and we can obtain the following result.

$$\begin{aligned} & \langle \sin 2\theta \sin(\varphi + \delta) \rangle_{AV} \\ &= \frac{1}{2\pi} \int_0^{2\pi} \sin 2\theta \sin(\varphi + \delta) d\varphi' \\ &= \frac{1}{8} \sin 2\theta_1 \sin(\varphi_1 + \delta) \end{aligned} \quad (13)$$

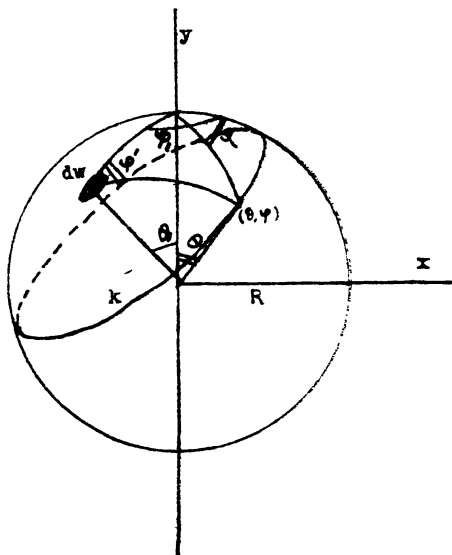


Fig. 1

Referring to equations (12) and (13), equation (11) i. e. the condition for a number of molecules in the small area $R^2 dw$ is constant, leads to the relation between α and du/dz , and at the same time, value of the constant δ is obtained.

$$\begin{aligned} du/dz &= (9u Z_m Z_c \nu \omega / 16\pi \rho R^3 Z_g kT^2) \exp(-\omega/kT) \\ \delta &= \pi/2 \end{aligned} \quad (14)$$

The Expression for the Viscosity Coefficient. If we denote by η the viscosity coefficient of a liquid, the shearing force F_x in equation (5) is equal to $\eta du/dz$. Then equations (7) and (14) lead the expression for η .

$$\eta = (32\pi \rho R^3 Z_g kT^2 / 45 Z_m Z_c \nu \omega) [(\partial P / \partial T)_v - Nk/V] \exp(\omega/kT) \quad (15)$$

We may consider Z_m/Z_g as the ratio of the number of occupied sites to that of total sites. In the case of approximation for the face-centered cubic lattice,

$$Z_g = 12, \quad Z_c = 4 \quad (16)$$

and the value for Z_m may be put at 10 without great error. When we use the density of lattice point $2^{1/2}/R^3$ for the density of total sites, then the density of molecules is given as follows:

$$\rho = 2^{1/2} Z_m / R^3 Z_g \quad (17)$$

By these relations expression (15) may be reduced to the following more or less simple form,

$$\eta = 0.787 (kT^2 / \nu \omega) [(\partial P / \partial T)_v - Nk/V] \exp(\omega/kT) \quad (18)$$

From this expression we can lead a formula which is quite alike that given by Eyring. We may neglect Nk/V when compared with $(\partial P / \partial T)_v$, since the latter is at least ten times larger than the former at an ordinary pressure. Furthermore we adopt the next well-known formulas concerning the molecular vibration ν and free volume v_f .⁽³⁾

$$\nu^{-1} = (2\pi m / kT)^{1/2} v_f^{-1/3}, \quad v_f = N^{-1} V^{-2} [2R / (\partial P / \partial T)_v]^3 \quad (19)$$

Then equation (18) becomes

$$\eta = KT^{5/2} M^{1/3} Q^{-1} V^{-2/3} \exp(Q/RT) \quad (20)$$

where $K = 8.4 \times 10^{-4}$ $R = \text{gas constant, cal/mol. deg.}$

(3) H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41** (1937), 249.

M = molecular weight, V = molar volume, cm^3 .

Q = activation energy for jumps, cal/mol.

Expression (20) obtained by the author differs somewhat from that of Eyring', namely, the latter has the term of heat of vaporization L_v instead of Q in the denominator of (20), i. e. it has a factor $(Q/L_v)K$ instead of K in equation (20). This difference has resulted from the different views on the relation between the flow and transition probability of a molecule. We may discuss the relative value of K of different liquids with a considerable degree of accuracy in spite of rough approximation as equation (19). The constancy of the value K for different liquids, especially in metallic liquids, each having a different and proper value of L_v/Q , is shown in Table 1. In this table the values of

Table 1.

	$\eta_m \times 10^3$	Q	L_v	L_v/Q	$K \times 10^4$
Na	7.9	0.96	25	26	5.4
K	5.5	1.15	21	18	3.8
Ag	4.4	4.87	59.5	12	3.1
Zn	33.4	2.92	24	8.2	3.7
Cd	25.3	1.59	26	16	4.0
Hg	20.1	0.598	14	23	3.9
Sn	20.3	1.603	78	49	3.5
Pb	28.5	2.32	46	20	3.2
Sb	14.6	2.92	45	16	2.0
Bi	18.6	1.715	46	27	2.7
Al	2.83	0.524	1.50	2.9	1.2
N_2	3.11	0.468	1.34	2.9	1.3
O_2	8.09	0.406	1.67	4.1	3.0
CH_4	2.25	0.740	2.20	3.0	1.1
C_2H_4	7.24	0.739			3.2
CO	3.21	0.463	1.41	3.1	1.6

The values of viscosity coefficients η_m at the melting points and that of Q and L_v have been taken from Ward's table.⁽¹⁾ Q and L_v are given in kilocalories per gram atom or gram molecule.

Q are obtained by the simple formula of Andrade's⁽⁴⁾ $A \exp(Q/RT)$, since we may neglect the temperature dependence of the term $T^{\frac{5}{2}} M^{\frac{1}{3}} Q^{-1} V^{-\frac{2}{3}}$ in expression (20) when compared with the rough approximation used in the course of derivation of this expression.

It may be said that Table 1 offers the experimental verification of the idea used in this paper.

(4) E. N. Da C. Andrade, *Phil. Mag.*, 17 (1924), 698.

(5) A. G. Ward, *Trans. Faraday Soc.*, 32 (1936), 88.

In conclusion the author would like to express his thanks to Dr. Y. Miyake and members of his laboratory for valuable discussions.

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On the Barrier Layer by the Contact between the Selenium Semiconductor and Metal. II.⁽¹⁾

On the Selenide Formation in the Barrier Layer.⁽²⁾

By Masao TOMURA.

(Received November 10, 1948.)

Introduction. It is well known that the barrier layer by the contact between the selenium and metal is the cause of rectification and barrier layer photoeffect. The author has already explained the formation, rectification and barrier layer photoeffect of pure contact when its barrier layer consists of selenium itself.⁽³⁾

The barrier layer of a practical selenium rectifier is not of a pure contact type, but composed of selenide as pointed out by the author.⁽³⁾ To improve the character of the selenium rectifier, more detailed studies on the structure of the barrier layer are desirable. Here the author will research the formation and structure of the barrier layer of a Cd-Se element.

Description of Experiments. The selenium purified by vacuum distillation is put on a base electrode in melting and it suffers a heat treatment of 4 hours at 200°C. Then cadmium is evaporated on the surface of selenium in vacuum and afterwards the cadmium film is covered with aluminium by the vacuum evaporarion to avoid tarnishing of cadmium at high temperatures.

The area of the element is 15 cm².

The element shows an electromotive force between the base electrode and front aluminium electrode, and it increases exponentially with temperature. Thus the current is picked up into the external circuit

(1) The previous report is in *Proc. Toshiba Lab.*, (in Japanese), **19** (1944), 206.

(2) Read at the annual meeting of the Phys. Soc. Jap. in Kyoto, (1948).

(3) M. Tomura, *Proc. Toshiba. Lab.*, (in Japanese), **18** (1943) 523, **19** (1944). 206.

and its characteristics are measured. The method of measurement is shown in Fig. 1. The current in the external circuit varies with the external resistance, so the latter is maintained as small as 25 ohms to pick up the former as much as possible. The current flows from the base electrode to the front electrode through the external circuit as shown in the figure in the same direction as the photocurrent of a selenium barrier layer photoelement. At first it amounts to about 100 micro-amperes at 100°C .

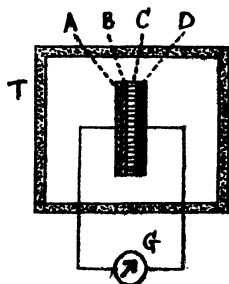


Fig. 1. Measuring apparatus.

- A Al electrode.
- B Cd film.
- C Selenium semiconductor.
- D Base electrode.
- G Galvanometer.
- T Thermostat.

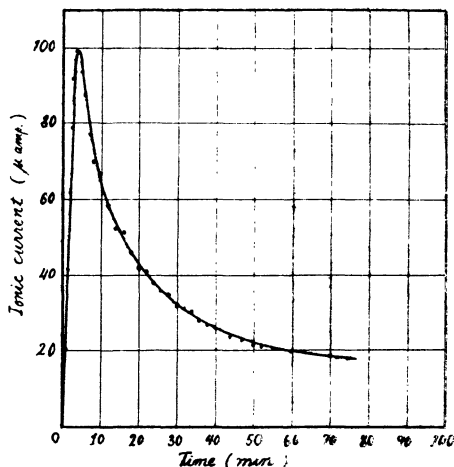


Fig. 2. Relation between the current and time

As the selenium semiconductor and both electrodes, as well as the copper lead wires, are kept at the same temperature, the current cannot be attributed to the so-called thermoelectromotive force by the temperature difference between them.

The relation between the current and time after bringing the element into the thermostat at 100°C is shown in Fig. 2. The initial steep increase of the current may mean the temperature rise of the element by its abrupt inserting into the thermostat, and the temperature of the element may reach 100°C after several minutes. Next, the current decreases with time and tends to zero asymptotically. The lower the temperature, in other words, the smaller the current, the more slowly decreases the current with time. For instance, the current does not decrease practically at room temperatures.

On the other hand, the resistance of the element becomes larger with the flow of current.

Next, the dependence of the current on the temperature is measured. As the current varies with time, cares are taken that the duration necessary to alter the temperature of the element does not influence results. Namely, the element is maintained long enough at the maximum

temperature 100°C necessary for the measurement, so that the current reaches to a practically constant value as shown in Fig. 2. And as the current becomes very small exponentially with the temperature decrease, and that makes the variation of current with time small as the above, the currents are measured in the course of the descending of temperature. Thus we can obtain the temperature dependence of the current avoiding the influence of the current decrease with time. Fig. 3. shows these results. The relation between the thermal current j and the absolute temperature T is found to be

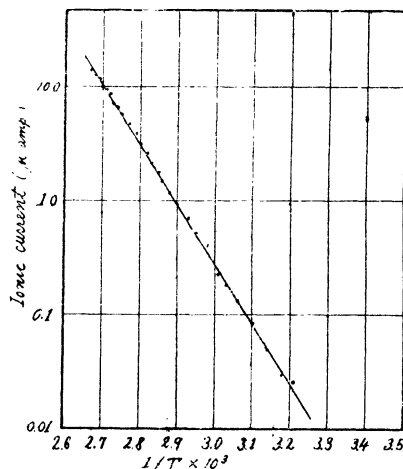


Fig. 3 Dependence of the current on the temperature.

$$j = j_0 e^{-\frac{\alpha}{T}}, \quad \text{or} \quad \log j = \log j_0 - \frac{\alpha}{T},$$

where j_0 and α are constants.

The static characteristics of rectification before and after the heat treatment are given in Fig. 4. The results show that the resistance of

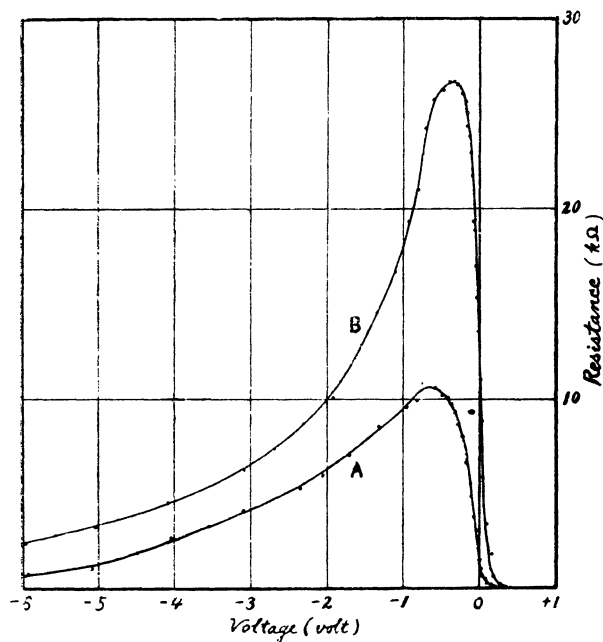


Fig. 4. Characteristics of rectification before (A) and after (B) the heat treatment of 100 min. at 100°C .

rectification of the element becomes very large by the heat treatment and furthermore the characteristics of rectification change by that treatment.

On the other hand, samples are made which have thin cadmium films of $10\sim 50\text{ m}\mu$ thick deposited by the vacuum evaporation on the selenium semiconductors. Their surfaces after the heat treatment of 4 hours at 210°C in vacuum are studied by the reflection method of electron diffraction. CdSe layers of the zinc blend type are observed on their surfaces.

Explanations of the Experimental Results. From the verification of the preceding section that the current observed is not attributed to any thermoelectromotive force, the cause of the current flow is none other than the converting process of the free energy difference in the reaction $\text{Cd} + \text{Se} \rightarrow \text{CdSe}$ to the electric energy, in order to keep the first law of thermodynamics. This assumption is supported by the experimental result obtained by the electron diffraction which shows the existence of CdSe layer on the surface of the sample, in other words, at the contact of the cadmium metal and selenium semiconductor.

From the fact that the current flows in this case, we can conclude that ions move just as in the electrochemical reaction, because an ionic crystal such as CdSe shows an ionic conduction in general by the moving of ions which are derived from lattice defects. Though the ionic conduction of CdSe has not been reported, we can assume as follows: since the ionic radius of Cd^{++} is $0.60\text{ \AA}$, and the one of Se^{--} $1.90\text{ \AA}$, the defect of Frenkel type is expected for CdSe and ionic charges are carried by the moving of cadmium ions through interstitial places of the lattice.

Since there exists an internal field of the order of 10^5 v./cm. at the contact of a Cd-Se element,⁽³⁾ the cause of the ionic current is that if a CdSe layer is formed by the direct reaction at the interface at first, the internal field acts upon that layer, making the cadmium ions at the interstitial points move to the selenium semiconductor side by the acceleration of the field. As the interstitial cadmium ions must take a distribution of a certain value at a given temperature, they are supplied from the cadmium electrode by the ionization of cadmium atoms into cadmium ions and electrons. The former move through the CdSe layer and the latter through the external circuit towards the selenium side, forming a new layer of CdSe. Thus the ionic current of the metal ion is observed in the external circuit. As will be mentioned afterwards, the mobility and number of the interstitial cadmium ions increase exponentially with temperature, the ionic current has the same nature, satisfying the result of Fig. 3.

The thickness of the CdSe layer becomes large with the flow of ionic current, consequently the field in the CdSe layer decreases and then the

current decreases with time as shown in Fig. 2.

The change of the rectification resistance of the barrier layer by the heat treatment shown in Fig. 4. supports certainty of the formation of the CdSe layer. By the transformation the barrier layer from one of pure contact to one of CdSe, the potential barrier at the interface becomes large for positive holes to go over the barrier, making the resistance of rectification large.

And the measurement of the abnormal spectral sensibility of a selenium barrier layer cell which has suffered a heat treatment supports the above explanation from the other side.⁽⁴⁾

Internal Field in the Barrier Layer which has a Selenide Layer.
The potential energy of an electron in the neighbourhood of the contact

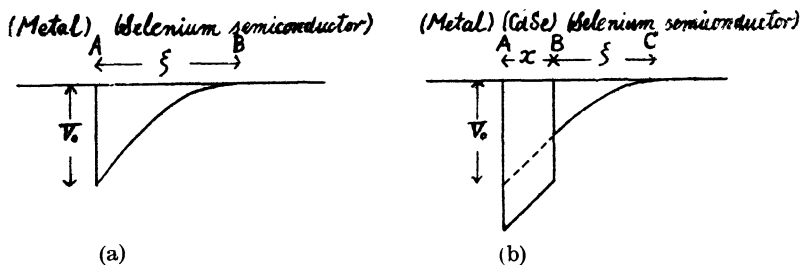


Fig. 5. Potential energy of an electron at the interface.

(a) The case of pure contact type.

(b) The case of selenide formation type.

V_0 is the contact potential difference between cadmium and selenium semiconductor.

is shown in Fig. 5. If we take N for the number of empty impurity centres in the unit volume of the selenium semiconductor and they are filled by the electrons from the metal when both elements are in contact, the potential energy of electron V is

$$\frac{d^2V}{d\xi^2} = \frac{4\pi Ne^2}{D}$$

Here e is the electronic charge and D the dielectric constant of selenium semiconductor. Then

$$\frac{dV}{d\xi} = \frac{4\pi Ne^2}{D} \xi \quad \text{and} \quad V = \frac{2\pi Ne^2}{D} \xi^2$$

are derived by taking ξ as the distance from the point B in Fig. 5 (a). If we put $1/L^2 = 2\pi Ne^2/V_0D$ into the above equations (L the thickness of the barrier layer of pure contact.), we get

$$V = \frac{V_0}{L^2} \xi^2 \dots\dots\dots (1)$$

(4) M. Tomura, This Bulletin, in the press.

and

$$\frac{dV}{d\xi} = \frac{2V_0}{L^2} \xi \dots\dots\dots (2)$$

where V_0 is the contact potential difference between both elements.

Next we take up the case in which a CdSe layer is growing. We assume that the CdSe layer is an insulator and there is no accumulation of charge at the interface between the CdSe layer and selenium. Thus if we take x as the thickness of the CdSe layer, we obtain

$$D \frac{dV}{d\xi} = D' \frac{dV}{dx} \dots\dots\dots (3)$$

by the continuity condition of field at the interface. Here D' is the dielectric constant of CdSe. From (2) and (3)

$$\frac{dV}{dx} = \frac{2V_0}{L^2} \frac{D}{D'} \xi \dots\dots\dots (4)$$

is derived. As the contact potential difference is distributed in the CdSe layer AB as well as in the selenium layer BC as shown in Fig. 5 (b), we get

$$\frac{2V_0\gamma}{L^2} \xi x + \frac{V_0}{L^2} \xi^2 = V_0,$$

namely,

$$\xi^2 + 2\gamma x \xi - L^2 = 0,$$

by considering (2) and (4), where γ is D/D' .

The solutions of the above equation are given by

$$\xi = -\gamma x \pm \sqrt{\gamma^2 x^2 + L^2},$$

but from the physical standpoint we must pick up the plus sign. Thus the field $F(x)$ in the CdSe layer is

$$F(x) = \frac{dV}{dx} = \frac{2V_0\gamma}{L^2} \{ \sqrt{\gamma^2 x^2 + L^2} - \gamma x \} \dots\dots\dots (5)$$

$$= \frac{2V_0\gamma}{L^2} x \left\{ \sqrt{1 + \frac{L^2}{\gamma^2 x^2}} - 1 \right\} \dots\dots\dots (5')$$

F has its maximum value $2V_0\gamma/L$ at $x = 0$ and tends to zero asymptotically with increase of x . γ may be nearly one, consequently in (5') if $L^2/\gamma^2 x^2 \ll 1$, namely $x \gg L$, we get

$$F(x) = \frac{2V_0}{L^2} x \left\{ \left(1 + \frac{L^2}{2x^2} - \frac{L^4}{8x^4} + \dots \right) - 1 \right\} = \frac{V_0}{x} \dots \dots \dots (6)$$

and in (5) if $\gamma^2 x^2 \ll L^2$ or $x \ll L$

$$F(x) = \frac{2V_0}{L^2} (L-x). \dots \dots \dots (7)$$

Theoretical Calculation of the Selenide Formation. If n is the number of cadmium ions per unit volume which move through the CdSe layer and u their mean velocity, the ionic current j per unit area is given by

$$j = nu. \dots \dots \dots (8)$$

The charge which is brought by the cadmium ions is proportional to the formation of CdSe, that is to say, to the thickness of CdSe, so

$$jdt = \alpha dx. \dots \dots \dots (9)$$

is given, where α is a constant. The number of lattice defects n is given by

$$n = n_0 e^{-\frac{W}{2kT}} \dots \dots \dots (10)$$

in the case of the Frenkel type⁽⁵⁾. W is the energy necessary to form a lattice defect and n_0 a constant. If U is the height of the potential barrier for the travelling of ions through the lattice, u is given by the next equation,⁽⁶⁾

$$u = \beta e^{-\frac{U}{kT}} \sinh \left(\frac{1}{2} \frac{ZeFa}{kT} \right) \dots \dots \dots (11)$$

Here β is a constant, Z the number of electronic charge of the ion, F the field in the crystal and a the distance between the neighbouring lattice sites.

Then from (8), (9), (10) and (11), we obtain

$$j = \alpha \frac{dx}{dt} = A e^{-\frac{\frac{1}{2}W+U}{kT}} \sinh \left(\frac{1}{2} \frac{ZeFa}{kT} \right) \dots \dots \dots (12)$$

as the equation of growth of the selenide layer.

Here A is a constant. Since Z is 2 for a cadmium ion, a , 2.62 Å. for CdSe of the zinc blend type and kT about 0.03 e.v. at 100°C, the value

(5) e. g. N. F. Mott and R. W. Gurney, "Electronic Process in Ionic Crystals", Oxford, (1940).

(6) Ibid.

of $\frac{1}{2} ZeFa/kT$ is $10^{-1} \sim 1$, even though we consider the maximum value $2V_0/L$ of F , because V_0 is about $0.5v$ and $L, 10^{-5} \sim 10^{-6}$ cm.⁽⁸⁾

Consequently, taking up the first term of the expansion of $\sinh\left(\frac{1}{2} ZeFa/kT\right)$, we can gain

$$j = a \frac{dx}{dt} = \frac{AeFa}{2kT} e^{-\frac{1}{2} \frac{w+v}{kT}} \dots\dots\dots (13)$$

Then the relation between t and x is

$$t = \frac{2akT}{Aea} e^{\frac{1}{2} \frac{w+v}{kT}} \int \frac{dx}{F(x)} \dots\dots\dots (14)$$

In the case of $x \gg L$, from (6) we get

$$\begin{aligned} t &= \frac{2akT}{Aea} e^{\frac{1}{2} \frac{w+v}{kT}} \int \frac{dx}{\frac{V_0}{x}} \\ &= \frac{akT}{AeaV_0} e^{-\frac{1}{2} \frac{w+v}{kT}} x^2 + C \dots\dots\dots (15) \end{aligned}$$

where C is an integration constant. So we obtain

$$j = a \frac{dx}{dt} = \frac{AeaV_0}{2kT} e^{-\frac{1}{2} \frac{w+v}{kT}} \cdot \frac{1}{x} \dots\dots\dots (16)$$

And if $x \ll L$, from (7) and (14) we get

$$t = \frac{2akT}{Aae} e^{\frac{1}{2} \frac{w+v}{kT}} \int \frac{dx}{\frac{2V_0}{L^2}(L-x)},$$

or

$$t = -\frac{akTL^2}{AaeV_0} e^{\frac{1}{2} \frac{w+v}{kT}} \cdot \log(L-x) + C'$$

Here C' is an integration constant and given as

$$C' = \frac{2kTL^2}{AaeV_0} e^{\frac{1}{2} \frac{w+v}{kT}} \cdot \log L, \text{ because } x = 0 \text{ at } t = 0.$$

Thus we obtain

$$t = \frac{akTL^2}{AaeV_0} e^{\frac{1}{2} \frac{W+U}{kT}} \cdot \log \frac{L}{L-x}, \dots\dots\dots (17)$$

or

$$x = L \left\{ 1 - \exp \left(- \frac{AaeV_0}{akTL^2} e^{-\frac{1}{2} \frac{W+U}{kT}} \cdot t \right) \right\} \dots\dots\dots (17')$$

namely,

$$j = a \frac{dx}{dt} = \frac{AaeV_0}{kTL} e^{-\frac{1}{2} \frac{W+U}{kT}} \cdot \exp \left(- \frac{AaeV_0}{akTL^2} e^{-\frac{1}{2} \frac{W+U}{kT}} \cdot t \right) \dots\dots\dots (18)$$

In Fig. 6. curves of $q (= \int j dt)$ versus t and q^2 versus t are plotted from the experimental data. As q is proportional to x , the curve q^2 versus t is satisfied by (15) except the region in which x is small. The

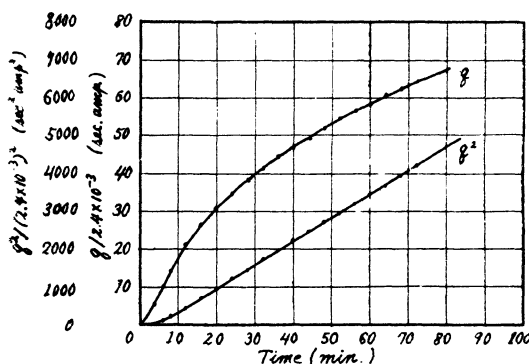


Fig. 6. q versus time and q^2 versus time curves.

region of the curve q versus t where x is small is satisfied by (17). But owing to the non-steadiness of temperature in the measurement when x or t is small, a rigorous analysis of the experimental curve in this region can not be made.

As stated above, the curve in Fig. 3 is obtained for the case in which the reaction of selenide formation progresses enough so that the CdSe layer grows thick. Then we can explain that curve by (16) which is derived for the case in which x or the thickness of the CdSe layer is large. (16) shows a linear relation between $\log j$ and $1/T$ at a given x . The activation energy of j is given as 0.98 e.v. from the experimental curve in Fig. 3. and corresponds to $1/2 W + U$ in (16). This value is allowable as one of a normal ionic conduction. The author has assumed that CdSe has defects of the Frenkel type, but the selection of another type of defects does not alter the mechanism of the selenide formation essentially.

From the presumption that the ionic current flows owing to the

internal field in the CdSe layer, (12) is substituted by

$$\sigma = \sigma_0 e^{-\frac{E}{kT}} \dots \dots \dots (19)$$

where σ is the ionic conductivity of CdSe and σ_0 is a constant. Assume the voltage impressed over the CdSe layer is nearly 0.5 v., because the internal field exists almost in the CdSe layer owing to the sufficient reaction in the experiment. Also assume the thickness of the layer $10^{-5} \sim 10^{-6}$ cm; σ_0 is derived as $10^3 \sim 10^4$ ohm $^{-1}$ cm $^{-1}$. from the experimental data in Fig. 3. This value is allowable for the moving of ions through an ionic crystal of the Frenkel type. From this magnitude of σ_0 , it can be concluded that the reaction takes place at the entire area of the interface and the ions do not move through only cracks of the crystal.

As a cadmium ion transports 2 electronic charges, the thickness of the CdSe layer estimated from the value of q at 60 min. in Fig. 6 is in the order of 10^{-8} cm.; considering the layer is uniform. This value is also probable for the case of heat treatment of one hour at 100°C.

Conclusion. The author found that a contact element of Cd-Se at elevated temperature had an electromotive force and the current caused by it was ionic, being attributed to the moving of cadmium ion through the CdSe layer accelerated by the internal field in the barrier layer to react with selenium.

Next the internal field in the barrier layer was calculated when the selenide formation took place and the experimental results were explained by the theoretical calculations of the formation of the CdSe layer at the contact.

Lastly, it must be pointed out that the selenide formation has an important rôle in the process of the third heat treatment in making a selenium rectifier.

The author thanks Mr. A. Otake for his co-operation in the setting of measuring apparatus.

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On the Diamagnetism of Perylene. I.

By Haruo SHIBA and Genjiro HAZATO.

(Received November 11, 1948.)

S. Banerjee⁽¹⁾ has measured the principal diamagnetic anisotropies along the three principal axes on various aromatic crystals. The diamagnetic value of the perylene crystal can be found in his paper, and this may be the only experimental one which we can see in the literature on this substance before the World War II. According to his result, the mean value of the three principal susceptibilities per mole of perylene becomes -159.6×10^{-6} . It is interesting that not only does this value deviate widely from Pascal's additive law, but also, as Banerjee had already pointed out, the diamagnetic anisotropy of this molecule is almost the same in magnitude with that of pyrene. As there are some other questionable points in this problem and as we fortunately had a specimen of perylene at hand, this measurement was newly attempted during the War. The result obtained by us showed somewhat larger diamagnetism than that of Banerjee's, and one of the values has already been published in another place briefly⁽²⁾. During the preparation of this paper, we have found in Chemical Abstracts the experimental value of this substance, reported by Pacault⁽³⁾ to be $\chi_M = -165.0 \times 10^{-6}$, where χ_M denotes mole susceptibility.

Synthesis of the Specimen and its Purification. The perylene used in this experiment had been prepared by the method of Hansgiring and Zinke⁽⁴⁾ by Prof. Kazuya Murata at Hiroshima Technical College, to whom we owe very much. It had been recrystallized alternatively from benzene and glacial acetic acid four times, and directly before the measurement, it was recrystallized once more from glacial acetic acid. Its melting point was 264° – 265° . A part of this sample sent to Zinke had been appreciated by him to be very pure.

Magnetic Measurements. We employed the apparatus of modified type of zero point method of Weiß und Foëx⁽⁵⁾, applying the constant field strength of about 6,000 gauß. The mass susceptibility of powdered naphthalene which had been purified by several recrystallizations and

(1) S. Banerjee, *Z. Krist.*, **100** (1939), 316.

(2) G. Hazato, *Kagaku (Iwanami)*, **14** (1944), 162, Table 3.

(3) A. Pacault, *Ann. chim.* [12], **1** (1946), 527; cf. *Chem. Abstracts*, **42** (1948), 4409

(4) F. Hansgiring and A. Zinke, *Monatsh.*, **40** (1919), 403.

(5) Refer, for example, to W. Klemm, "Magnetochemie," p. 46, Leipzig (1936).

sublimations, and that of purified water were chosen as standards, assuming their values to be -0.717×10^{-6} and -0.720×10^{-6} , respectively. The principle of this method lies in comparing the repulsive force, induced by the constant magnetic field in each gram of the specimen, with that of the standard substance, assuming the proportionality between the mass susceptibility and the corresponding repulsive force.⁽⁵⁾

Both naphthalene and specimen were powdered as fine as possible, and about 0.3 g. of each of them was crammed into the globular part of quartz vessel A, which is shown in Fig. 1. The vessel A is jointed

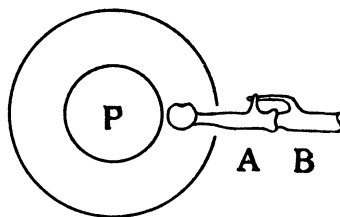


Fig. 1.

to the end of the quartz tube B held horizontally by two bifilar suspensions⁽⁵⁾, and P shows the poles of the magnet. When A is connected to B, the two projections situated at each end of A and B are adjusted so as to be in contact with each other at the same position. In this manner, we can always reproduce the same relative position of the sample to the magnetic poles.

The repulsive force mentioned above can be measured by the magnitude of the counter force applied against the repulsive one so as to bring back the specimen to the original zero point by means of a weak direct current passed through the secondary coil which is situated at the other end of the quartz tube B⁽⁵⁾. The reading of the microammeter inserted in the circuit of the secondary coil ought to be proportional to the repulsive force, namely the product of the mass susceptibility and the weight of the sample.

The results obtained are as follows:

Table 1.

	Substance	Weight of Substance (g.)	Reading of Ammeter ($\mu A.$)	$-\chi_g \times 10^5$	$-\chi_M \times 10^5$
(a)	Water	0.4326	24.8	0.720 (standard)	
	Perylene	0.3530	19.0	0.676 (obtained)	170.4
(b)	Naphthalene	0.3136	17.7	0.717 (standard)	
	Perylene	0.3530	19.0	0.684 (obtained)	172.4

where χ_g and χ_M denote the mass and mole susceptibilities respectively.

Brief Considerations. If the configuration of perylene is considered to consist of two naphthalene nuclei combined at both the peri-positions, the magnetic susceptibility of this molecule may be calculated from that of naphthalene as follows:

$$\begin{aligned}\chi_M(\text{Perylene}) &= 2\chi_M(\text{Naphthalene}) - 4\chi(\text{H}) \\ &= -171.8 \times 10^{-6},\end{aligned}\quad (1)$$

assuming that,

$$\chi_M(\text{Naphthalene})^{(6)} = -91.77 \times 10^{-6}$$

and

$$\chi(\text{H})^{(7)} = -2.93 \times 10^{-6}.$$

The value obtained in (1) coincides closely with our experimental ones shown in Table 1. Accordingly, we can say that the additive law is also nearly correct in the case of perylene, if we neglect the so-called "constitutive corrections for the trinuclear and the binuclear carbons" with regard to the central hexagon. This result shows that in perylene molecule the two naphthalene nuclei are playing a predominant role, and the central nucleus (C in Fig. 2) seems to have a special structure, having no correction term to be added for its own sake. If it were not so, the correction terms for the trinuclear carbons and for the binuclear ones would have to be added according to Pascal's additive law⁽⁷⁾. If these corrections were added, the resulting value would become -185.2×10^{-6} , which lies far from the experimental one. As a matter of fact, however, it is natural to consider that the origin of the correction terms for "the trinuclear and binuclear carbons" may rather be ascribed to the conditions of the planar structure of the molecular orbits in aromatic network, than to the specific character of individual carbon atom.

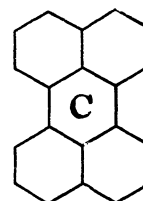


Fig. 2

On the other hand, it can be considered that aromatic molecule, in general, consists of two parts of diamagnetism, viz. the one is isotropic and the other anisotropic. The isotropic part will be represented by K_1 or K_2 , showing the mole susceptibility of aromatic compounds when the molecular plane is situated parallel to the directions of the magnetic field; in this condition the anisotropic part vanishes. Let the anisotropic part per mole be ΔK , the following relationship will be satisfied,⁽⁸⁾

$$\Delta K = K_3 - K_1.$$

Here, K_3 represents the susceptibility when the molecular planes are put perpendicular to the direction of the magnetic field. Then in the case

(6) International Critical Tables.

(7) Cf., for instance, S. S. Bhatnagar and K. N. Mathur, "Physical Principles and Applications of Magnetochemistry," p. 90-92, London (1935); W. Klemm, "Magnetochemie," p. 160-161.

(8) L. Pauling, *J. Chem. Phys.*, **4** (1936), 676.

of fine powdered crystals, the mean susceptibility per mole becomes

$$\chi_M = K_1 + \frac{1}{3} \Delta K, \quad (2)$$

because of the planar structure of the molecule.

Accordingly, we can deduce ΔK from the equation (2), knowing the numerical value of K_1 . To evaluate K_1 approximately, it is convenient to use the following modification of Pascal's additive law:⁽⁹⁾

$$K_1 = \sum \chi(C =) + \sum \chi(H), \quad (3)$$

where, $\chi(C =)$ denotes the atomic susceptibility of the unsaturated carbon including the constitutive correction of half a double bond; the numerical values are⁽⁷⁾

$$\left. \begin{aligned} \chi(C =) &= \chi(C) + \frac{1}{4} \chi(C = C - C = C) \\ &= \left(-6 + \frac{1}{4} \times 10.56 \right) \times 10^{-6} = -3.36 \times 10^{-6} \\ \chi(H) &= -2.93 \times 10^{-6} \end{aligned} \right\} \quad (4)$$

Applying these values in (3) and (2) in combination with the experimental values of χ_M , we can calculate ΔK for various aromatic molecules. Taking the value of ΔK of benzene as the unit, we can evaluate the relative anisotropies of various aromatic hydrocarbons, the results being summarized in Table 2 together with those by other authors⁽¹⁰⁾⁽¹¹⁾

Table 2.

Substance	$-\chi_M \times 10^3$	Relative Anisotropies		
		Obs. (powd.)	Obs. (s.c.) ⁽¹⁰⁾	Theo. (L.) ⁽¹¹⁾
Benzene	55.1	1	1	1
Naphthalene	91.8	2.0	2.11	2.18
Anthracene	129.2	3.05	3.38	3.45
Phenanthrene	127.9	2.97	3.07	3.19
Pyrene	147.9	3.74	4.31	4.46
Diphenyl	104.9	2.0	2.20	2.21

Here, Obs. (powd.) indicates the results obtained in the present case, and χ_M the experimental susceptibilities of powdered crystals or liquid obtained by Pascal. Obs. (s. c.) shows the results obtained by Lonsdale and Krishnan on the single crystals except in the case of benzene. Theo. (L.) shows the pure theoretical ones obtained by London.

(9) G. Hazato, *J. Chem. Soc. Japan*, **64** (1943), 483.

(10) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. (London)*, **A**, **156** (1936), 597.

(11) F. London, *J. de Physique*, **8** (1937), 397; *J. Chem. Phys.*, **5** (1937), 837.

In the analogous manner, we can deduce the relative anisotropy of perylene to naphthalene from the results of Table 1, i. e.

$$\Delta K \text{ (Perylene)}/\Delta K \text{ (Naphthalene)} = 1.96-2.02. \quad (5)$$

This result coincides well with that of the relation (1). The relative anisotropic values shown in Table 2 correspond approximately with the number of benzene nuclei. And from this result it may analogously be deduced that ΔK of perylene is rather 2.5 times that of naphthalene, but contrary to the supposition, the result of observation indicates as if two naphthalene nuclei predominated in the perylene molecule. If the ΔK of perylene were 2.5 times as large as that of naphthalene, $-\chi_M \times 10^6$ of perylene would be 187, which deviates widely from the experimental one.

In spite of the above mentioned discussions, there still remain many questions which we have to discuss further in detail. It may be certain, however, that from the structural point of view, the perylene molecule has essentially two predominant naphthalene nuclei, of which both the peri-bonds are somewhat longer than that of the carbon bond in benzene nucleus, but are not pure single bonds. This argument will prove to be correct, if the theoretical treatment of London⁽¹⁰⁾ is modified a little. Details of it will be mentioned in the following articles.

Summary.

The diamagnetic susceptibility of perylene in powdered form has been measured and found to be $-(171 \pm 1) \times 10^{-6}$ per mole, and from this value the structure of perylene is discussed. A simple method has also been proposed to evaluate the anisotropic part from the mean molecular susceptibilities of aromatic molecules. The present result shows that perylene molecule has two predominant naphthalene nuclei and the central hexagon in this molecule has a special structure as compared with the other four.

The present writers wish to express their sincere thanks to Prof. H. Tominaga, Director of the Institute, for his kind advice and encouragement throughout this investigation. These experiments have been realized by "the Bounty for Natural Science in 1943" afforded by the Ministry of Education to one (H. S.) of the writers.

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Flame Length and its Heat Radiation.

By Sakae YAGI.

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This contribution involves our studies on flames during these ten years: Studies on Luminous Flames⁽¹⁾, Studies on Turbulent Diffusion (Flame Length)⁽²⁾, and Studies on Flame Radiation⁽³⁾. In spite of wide application of flames for heating both in industrial and scientific purposes, few studies had been published particularly for design use.

The burner used in our measurement of flame length and radiation is shown in Fig. 1. Fuel gas compressed in a tank is flowed through a stream straightner and lighted at a burner nozzle, whose opening or diameter can be changed from 1 mm. to 10 mm.

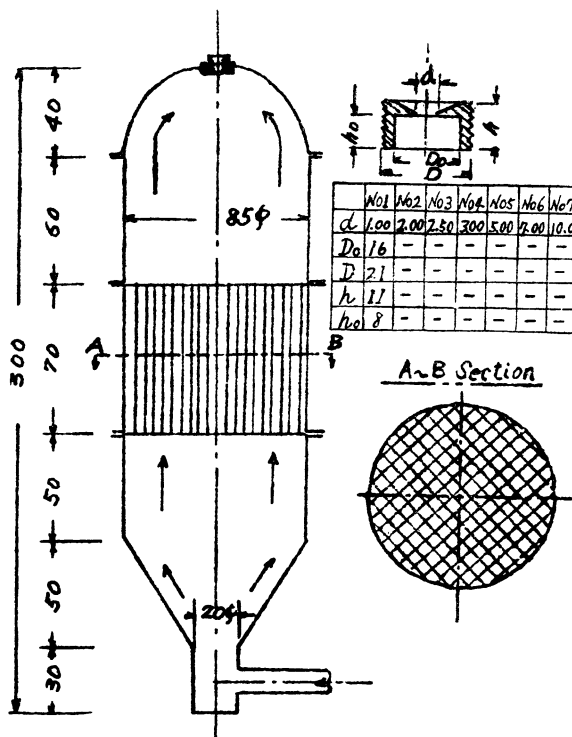


Fig. 1. Burner for measurement.

Measurement of Flame. Length of flame is measured by the picture taken in front of a bright scale background as shown in Fig. 2. Relationship between (flame length L cm.)/(nozzle diameter d cm.) and (Fuel gas velocity at nozzle opening u cm./sec.) $\times (d$ cm.) is summarized as Fig. 3 with several sizes of nozzle diameter. At the lower value of ud , L/d increases almost proportionally to ud and at the higher ud , L/d is almost independent of ud , tending to $L/d = 50-70$.

(1) J. Soc. Chem. Ind., Japan, 1937, 90, 93, 263.

(2) J. S. C, I. J., 1943, 608, 821, 837.

(3) J. Chem. Soc. Japan, Ind. Ed., 52 (1949), 167.

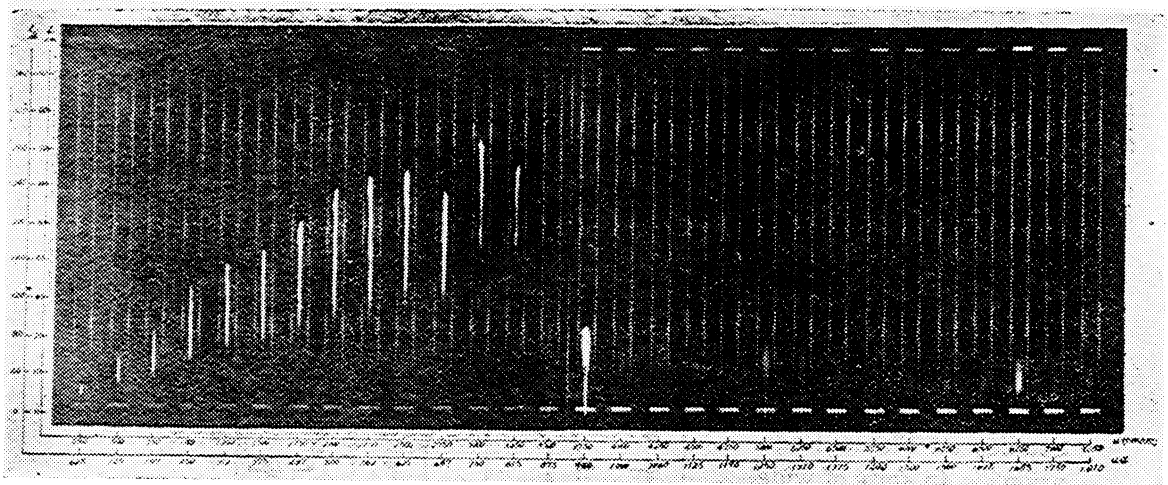


Fig. 2. Flame length of 4 mm. nozzle.

The two states of flame above mentioned are also observed by the photographic observation of flame (Fig. 2): one is a diffusal flame or laminar flow flame and the other a turbulent flame, and there can be seen some transitional region between the two states⁽⁴⁾.

Theoretical Consideration of Burning Rate. We can establish the following equation of material balance, if a flame in cylindrical form is assumed to be mixing status of air to fuel gas by means of molecular or turbulent diffusion, which means that the chemical reaction rate of combustion is assumed to be very large compared with the mixing rate,

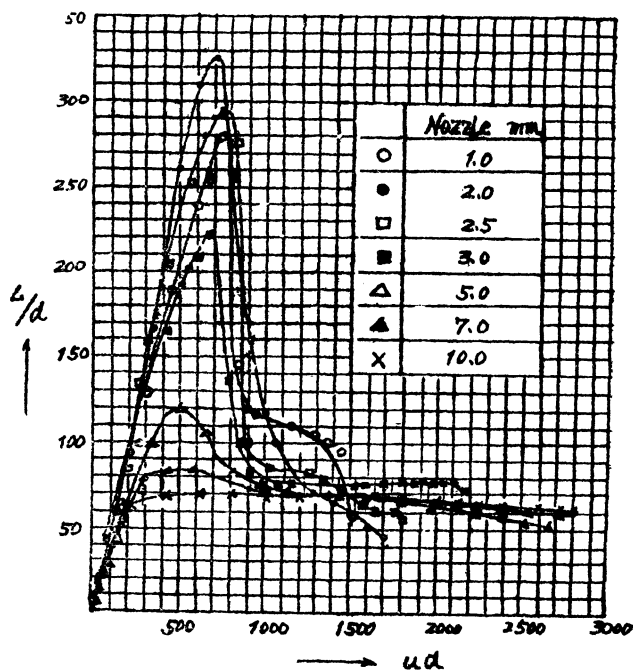


Fig. 3. Flame length.

$$\pi d^2 \frac{dc}{4 dx} u = \pi d \frac{D + \epsilon}{\delta} \Delta c \dots \dots \dots (1)$$

(4) S. Yagi, J. S. C. I. J., 1943, 873.

wherein d is diameter of flame, c : concentration of fuel in flame, D , ε : molecular and turbulent diffusion constant $\text{cm}^2/\text{sec.}$ of air into flame through a layer length $\delta \text{ cm.}$, u : velocity of flame gas cm./sec. , x : length from burner nozzle. The above equation can be integrated by using average value of u , D , ε at the boundary condition of ordinary atmospheric combustion: $\Delta C = C$, $C = C_i$ at $x = 0$

$$\frac{C}{C_i} = e^{-\frac{4(\bar{D} + \bar{\varepsilon})}{\bar{u}d\delta}x} = e^{-Kx} \dots \dots \dots (2)$$

$$K = 4(\bar{D} + \bar{\varepsilon})/\bar{u}d\delta \dots \dots \dots (3)$$

As the fuel concentration at the top of the flame measured was analysed as some figure like $0.1C_i$, the flame length L can be calculated by putting $C/C_i = 0.1$ and $x = L$ in equation 2.

$$\frac{L}{d} = \left(\frac{2.3}{4}\right) \frac{\bar{u}d\delta/d}{(\bar{D} + \bar{\varepsilon})} \dots \dots \dots (4)$$

$\bar{\varepsilon}$ was calculated at the jet nozzle by solving the Tollmien equation⁽⁵⁾ as $2 \times 10^{-3} u_0 d_0$, where u_0 and d_0 are jet velocity and diameter⁽⁶⁾. Comparing the result of flame length measurement (Fig. 3) with equation 4, we get the following conclusions:

1. For diffusional flame:

Theoretical calculation under condition that $\bar{\varepsilon} = 0$

$$\frac{L}{d} = \left(\frac{2.3}{4}\right) \left(\frac{\delta/d}{\bar{D}}\right) \bar{u}d \dots \dots \dots (5)$$

Measured result according to nozzle diameter

$$L/d = (0.3 \sim 0.5)ud$$

Probable values of unknown figures

$$\delta/d = 2.0 \sim 1.2 \text{ changing at various } d$$

if $D = 2.4 \text{ cm}^2/\text{sec.}$ at air diffusing through city gas at 1200°K

2. For turbulent flame at above $500 \text{ cm}^2/\text{sec.}$ of ud

Theoretical calculation under condition that $\bar{\varepsilon} = 2 \times 10^{-3} u_0 d_0$ and $\bar{D} = 0$

$$L/d = (290) (\delta/d) u_0 d_0 / \bar{u}d$$

Measured average result of larger diameters

(5) Z. f. angew. Math. u. Mech., 1926, 468.

(6) S. Yagi, J. S. C. I. J., 1943, 603.

$$L/d = 60 \dots\dots\dots(6)$$

Probable values of unknown figures

$$(\delta/d)(u_0 d_0 / \bar{u} d) = 0.2$$

at extreme turbulence.

3. For transitional flame :

Unable to be established definitely.

Effect of Primary Air. Although primary air in the burner frequently causes increase of combustion rate, it is not always that flame length decreases by addition of primary air as shown in Fig. 4.

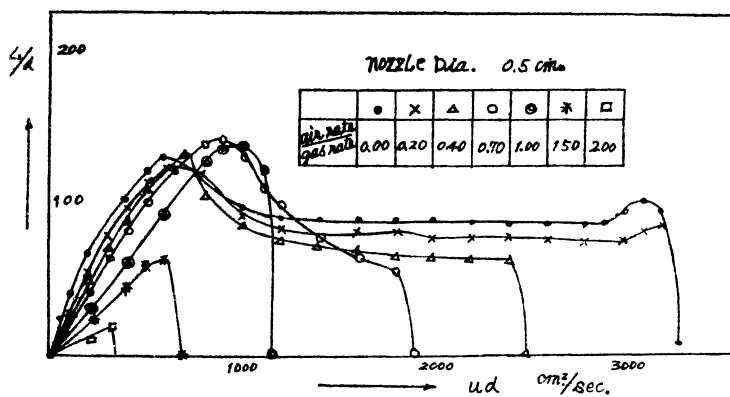


Fig. 4. Flame length adding primary air.

An important influence of adding primary air is that high primary air makes the blow limit of the gas burner have a smaller amount of ud , that means decrease in the capacity of the burner.

Further description and discussions will be available in "Flame Length III"⁽⁷⁾.

Radiant Heat from Flame. The radiation from the flame of the above mentioned burner was measured along the length of the flame by a sensitive thermopile and galvanometer, which was calibrated with a standard black body furnace. The results measured are shown in Fig. 5, where Q_f is flame radiation integrated along the whole length of the flame, V_f is gas volume nl/h. The experiment was conducted with various openings of the burner nozzle, i.e. 1, 2, 5, 7, 10, mm. and various kinds of fuel gas, i.e.

I: City gas only of 3000 Kcal./nm.³,

II: City gas added with C₂H₂ 6 vol. %,

(7) S. Yagi and T. Kimura, J. Chem. Soc. Japan, Ind. Ed., 1949, in printing.

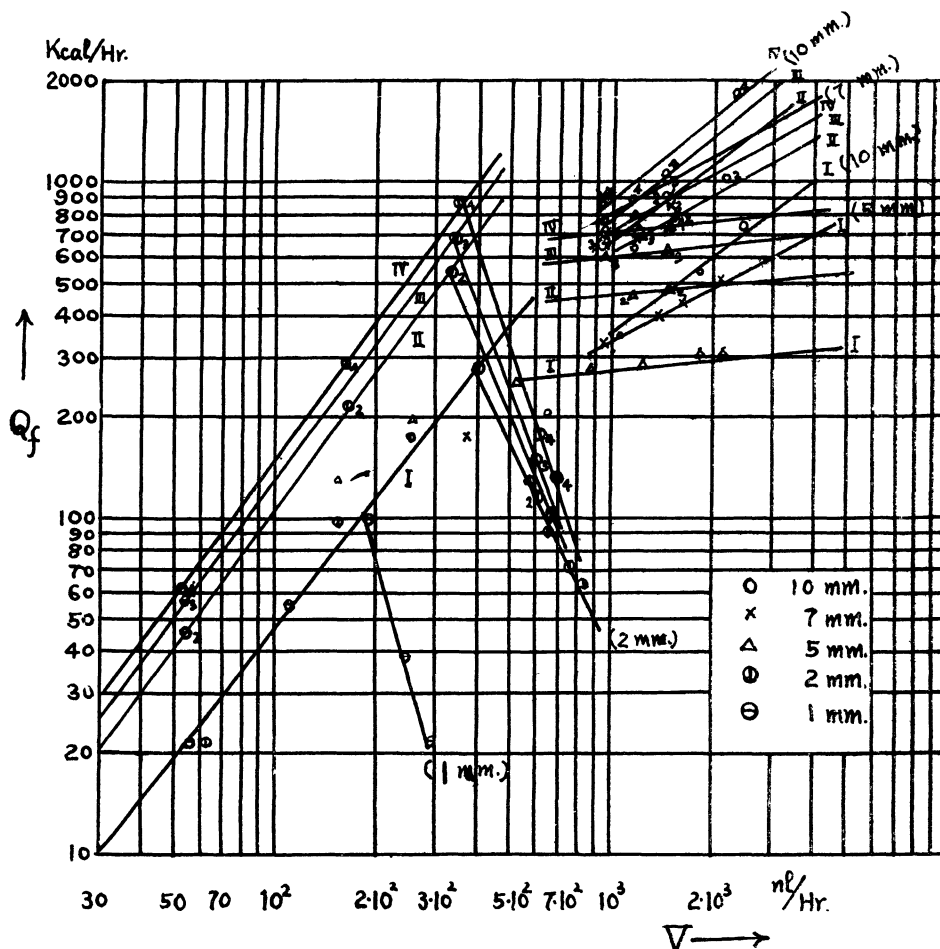


Fig. 5. Radiation from flame.

Curve I: Town Gas only.

Curve II: Town Gas plus 6% C_2H_2 .Curve III: Town Gas plus 8% C_2H_2 .Curve IV: Town Gas plus 10% C_2H_2 .III: City gas added with C_2H_2 8 vol. %,IV: City gas added with C_2H_2 10 vol. %,

In the laminar flow flame, the radiant heat Q_r is independent of burner opening, which is expressed as

$$Q_r = K(1 + aw)V^{1.25} \dots \dots \dots (7)$$

where K and a are constants, and w is the fraction of acetylene volume. In the turbulent flame Q_r decreases rapidly for smaller d and, in so far as the larger burner is concerned, Q_r is approaching the line of $Q_r = K'(1 + a'w)V$, which means that the industrial large burner gives such an

amount of radiant heat as

$$Q_r = K'(1 + a'w)V \dots\dots\dots(8)$$

The percentage of the amount of heat emitted per total heat content of fuel used, η , varies with ud and d as shown in Fig. 6. By means of data on the 10 mm. burner, it will be supposed that the larger burner for industrial use will give some definite value of η , as 10 % in the 10 mm. burner. Detailed data will be shown in "Radiant Heat from Flame" ⁽⁸⁾.

Spectral Radiation of Luminous Flames. The author studied the absorption spectra of soot and luminous flames ⁽⁹⁾. The burner was made for the convenience of measuring emission and absorption spectra. Absorption spectra of soot plate and luminous burning soot are expressed as

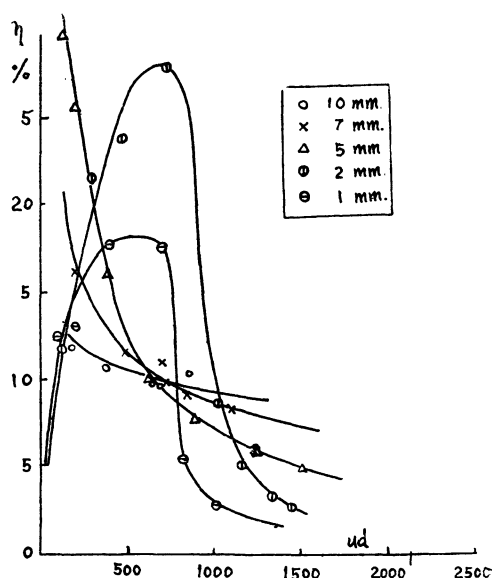


Fig. 6. Percentage of radiation.

$$kl = 39.5 \nu N l (1 - 15[\rho\nu]^2) \dots\dots\dots(9)$$

where k is the absorption coefficient of soot cm.^{-1} , l the thickness of flame, ρ radius of a soot particle in μ , N number of particles in cm.^3 , ν the wave number of spectra $\text{cm.}^{-1} \times 10^4$. The above formula was derived from the theoretical standpoint of colloidal soot particle.

The results of the experiment are shown in Fig. 7a, Fig. 7b and Fig. 8. On adding benzene vapor to city gas, spectral radiation increases as shown in Fig. 7a as I, II, III and N in equation 9 increases proportionally as shown as equations in Fig. 7b. Fig. 8 denotes flame radiation and soot radiation (thick line) and the equivalent black body radiation (thin line), of which the soot radiation was calculated from soot equations in Fig. 7b, referring to the transparent region of gas absorption, and the black body emission was calculated by dividing the emission energy with absorption data. The thin broken line shows the ideal black body emission. The differences between full and broken lines in both

(8) S. Yagi, S. Yoshida and M. Yorizane, J. Chem. Soc. Japan, Ind. Ed., 52 (1949), 167.

(9) S. Yagi, J. S. C. I. J., 1937, 90, 93, 267.

flame and black body emissions show the emission and absorption of CO_2 and H_2O in flame and surrounding atmosphere, whose temperatures are not the same as soot temperature. Therefore the two smooth curves are thought to have meaning of theoretical standard. Similar results were obtained, as described in the original contributions, in flames with added acetylene and primary air.

The effective temperatures concerning heat

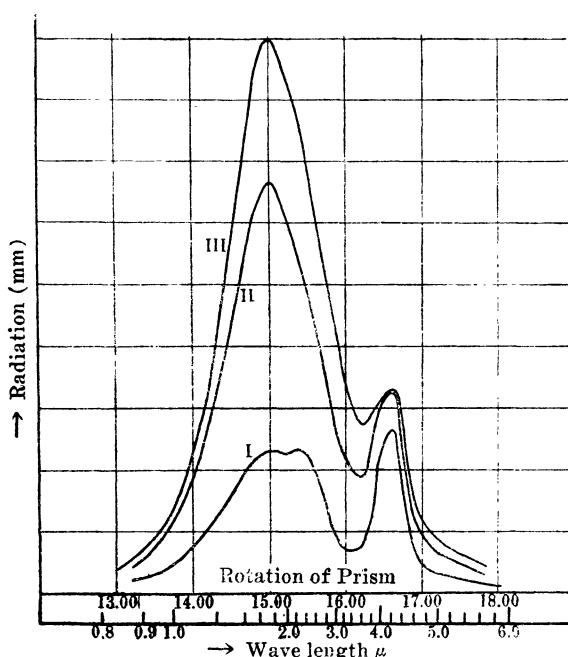


Fig. 7a. Radiation spectra of luminous adding benzene vapor

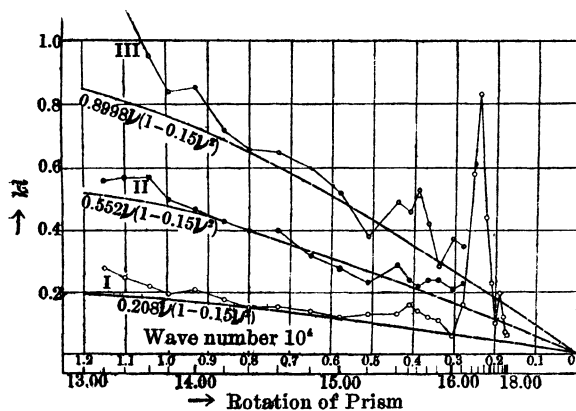


Fig. 7b. Absorption spectra of luminous flame adding benzene vapor.

	I	II	III
		C_6H_6	
Hydrocarbon %	0	1.95	3.46
Town gas cc./mm.	144	106	100

radiation were calculated from the distribution of black body emission as shown in the following table compared with data measured by ordinary optical pyrometer and figures

corrected from absorption $650 \text{ m}\mu$ in parenthesis below.

Table 2. Temperatures of Several Luminous Flames.

Adding Primary Air (%)	Temp. (°C)		Adding C_2H_2 (%)	Temp. (°C)		Adding C_2H_6 (%)	Temp. (°C)	
	from F'	Opt. Pyro.		from F'	Opt. Pyro.		from F'	Opt. Pyro.
0.0	1280	1370 (1450)	0.0	1360	1260 (1420)	0.0	1360	1260 (1420)
13.6	1330	1440 (1630)	3.76	1400	1400 (1515)	1.95	1260	1390 (1480)
20.8	1470	1250 (1480)	8.06	1330	1380 (1460)	3.46	1220	1320 (1440)

The temperature increases by addition of primary air and decreases by addition of hydrocarbon. The data measured by optical pyrometer even after the correction can not show the effective temperature of radiation, but seems to show some temperature of soot particles suspending in the zone of some high temperature but of relatively thin layer.

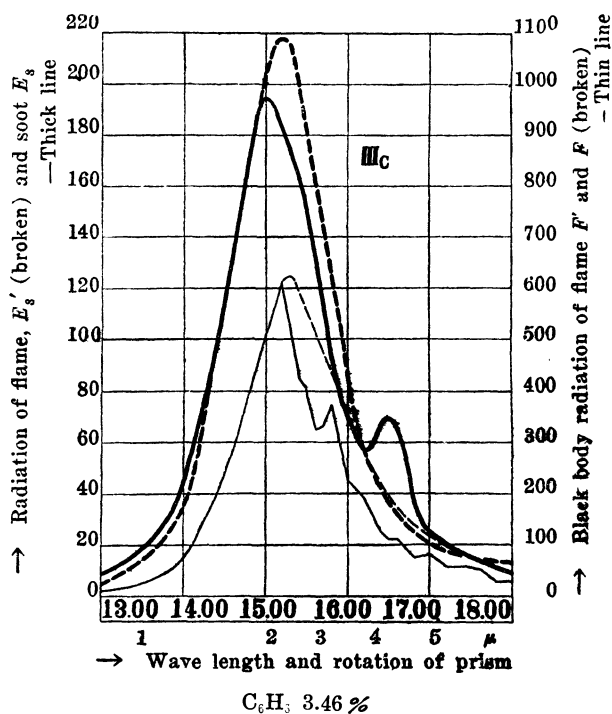


Fig. 8.

The major part of this series of work was conducted in the Tokyo Institute of Technology with collaborators and some in the Massachusetts Institute of Technology under Prof. H. C. Hottel, to whom the author wishes to express his indebtedness.

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A New Chemical Method for Measuring the Ultra-violet Ray.

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1. There have been several methods to measure the ultra-violet ray using the photochemical reaction of solution. Among them, the methylene blue-acetone method contrived by Webster, Hill and Eidinow⁽¹⁾ and the uranyl acetate-oxalic acid method by Moss and Knapp⁽²⁾ are well known. When these mixed reagents are irradiated with the ultra-violet ray, photochemical reactions take place which are more or less proportional to light energy. Thus, relative intensity of light may be obtained by quantitative determinations of reaction products.

But, as these reactions are not so sensitive and since at least ten to thirty minutes are necessary for the time of exposure, they are not useful for following a rapid change or measuring weak ultra-violet ray. For these purposes, the photochemical reaction of the leuco-base of triphenyl-methane dyestuff seems to be the most promising.

In fact, I. G. Farbenindustrie in Germany offered Bioklimatische Ultra-violet Dosimeter using a colorless sulfite of fuchsin. However, it has not sufficient sensibility to measure quickly weaker radiation. The author's intention has been to make more sensitive ultra-violet radiation from the sun and the sky using the photochemical reaction of the leuco-base of crystal violet.

2. Lifschitz⁽³⁾ found that when colorless cyanide or sulfite of triphenyl-methane dyestuff is irradiated with the ultra-violet ray, the color of the original dyestuff develops immediately which gradually disappears again in the dark.

E. Weyde and W. Frankenburger⁽⁴⁾ studied the photochemical behavior of leuco-bases of crystal violet. According to them, the rate of coloration of the leuco-base by ultra-violet ray is proportional to the quantity of light energy. The quantum yield of this photochemical reaction is almost nearly 1 in the region from 3135 Å to 2537 Å, and the maximum sensibility lies at about 2700 Å. The temperature coefficient of the reac-

(1) L. Hill, *Proc. Roy. Soc.*, A 114 (1927), 265.

(2) Moss and Knapp, *J. Soc. Chem. Ind. Trans.*, 44 (1925), 453.

(3) Lifschitz, *Ber.*, 52 (1919), 1419; 61 (1928), 1463; Lifschitz and Joffe, *Z. physik. Chem.*, 97 (1921), 426; Lifschitz, *Z. wiss. Phot.*, 29 (1930), 91.

(4) E. Weyde and W. Frankenburger, *Trans. Faraday Soc.*, 27 (1931), 561 (The Photochemical Processes. A General Discussion.); E. Weyde, W. Frankenburger and W. Zimmermann, *Z. physik. Chem.*, B 17 (1932), 276; *Naturwissenschaften*, 18 (1930), 206.

tion is also practically 1 in the range from -6° to $+40^{\circ}\text{C}$.

We have made an instrument for measuring the ultra-violet radiation using the cyanide of crystal violet as follows:

5 c.c. of the saturated solution of the leuco-base in absolute alcohol is sealed in a quartz glass ampule with an inner diameter of 13 mm. and length of 9 cm. Ten other hard glass ampules of the same size are each charged with 5 c.c. of the alcoholic solution of pure crystal violet. These are used as colorimetric standards. The concentration of the latter solution is $1.72 \times 10^{-5} \times (2/3)^n$ mol/litre where n is a positive integer from 0 to 9 respectively. As the solubility of the leuco-base in absolute alcohol is 5.8×10^{-5} mol/litre at room temperature, 1.72×10^{-5} mol/litre is equal to its 8/27.

We define a color standard with the concentration $n = 0$ as grade 10 and successively, $n = 1$ as grade 9, and so on. Measurement of light intensity is done as follows.

When an ampule containing the leuco-base solution is exposed to light for five to sixty seconds, a violet color appears. The ampule is shaken during exposure so as to mix the solution well. The time of exposure is measured with a stop watch. Then it is quickly compared with color standards protecting against the ultra-violet ray completely. When a depth of color thus attained falls between those of two color standards, the grade is read to a fractional number.

The depth of color should be proportional to the quantity of light energy received in the solution which is the product of time of exposure (t), light intensity and the surface area. Therefore, even for the same intensity of light, coloration of leuco-base solution would be different with a different time of exposure. We must reduce the coloration to that which would be obtained for a definite time exposure. Hence, we define the normal grade as a grade of color which develops when the leuco-base solution is exposed to the ultra-violet ray for just sixty seconds.

In actual cases, the time of exposure is not usually sixty seconds, so we reduce a grade of color directly observed to the normal grade to compare its light intensity with others. Let G be the normal grade, G_t , a grade obtained directly in an observation and t , time of exposure in seconds, G is calculated from the following equation.

$$G = G_t - (\log t - \log 60) / \log 3/2 \quad (1)$$

When G is thus calculated, relative intensity of light may be easily obtained as described in the next section.

3. There is a following relation between the normal grade G and the light intensity $E(\text{erg/cm}^2 \cdot \text{min.})$

$$\log E = \log \kappa + (G - 1) \cdot \log 3/2 \quad (2)$$

where κ is a constant depending on the wave length of light etc.

In the case of monochromatic ray, the light energy E consumed for the photochemical decomposition of the leuco-base is expressed in the following formula;

$$E = m N h \nu / s t \quad (3)$$

where m is the number of mol of dyestuff formed; N , avogadro's number; h , Planck constant; ν , the frequency of light wave; s , the area of irradiated surface of solution, 25 cm².; t , time of exposure in minutes. This formula holds only in the ideal case where the quantum yield is 1 and the dark reaction is negligible. But for practical purposes, the leuco-base solution is made so as to finish the dark reaction in fifteen to thirty minutes, therefore, the rate of dark reaction can not be regarded as negligible. Moreover, the presence of impurities in reagents and the formation of a yellow decomposition product of unknown composition disturb the photochemical reaction. It is impossible to estimate these causes of error quantitatively.'

The loss of light energy by reflexion and absorption may be estimated approximately as follows. According to L. Harris and J. Kaminsky⁽⁵⁾, the rate of reflexion between the interface of the air and the quartz glass is 0.094 % at 3130 Å and at the interface between alcohol and quartz glass it is about 0.0004 %. Thus, the total depletion by reflexion is not more than about 0.09 %.

Let intensity of normal incident light be I_0 , then intensity of transmitted light I is,

$$I = I_0 \times 10^{-K \cdot c \cdot d} \quad (4)$$

where K is the absorption coefficient of the leuco-base solution, 3.16×10^{-4} ; c , its concentration, 5.8×10^{-5} mol per litre; d , depth of liquid. As the solution is contained in an ampule, the depth of liquid is.

$$d = 2 \{ r^2 - (\alpha r)^2 \}^{\frac{1}{2}} \quad (5)$$

where r is the inner radius of an ampule, 6.5 mm.; and α is a variable between 0 at the margin and 1 at the center of the ampule. From the above formulae, we obtain approximately 1.9 % as the mean value of absorption. Therefore, it may be said that about 2 % of light energy is lost by reflexion and absorption before the formation of dyestuff begins. After the dyestuff is formed, it will act as an absorber of light, the rate of which is proportional to its concentration.

Since radiation from ordinary light sources, for example, quartz mercury lamp, the solar radiation etc., is by no means monochromatic,

(5) L. Harris and J. Kaminsky and R. G. Simard, J. Am. Chem. Soc., 57 (1935), 1151.

the light energy can not be calculated simply by the formula (3). In short, the quantitative determination of the ultra-violet ray is impossible due to complicated sources of uncertainty as explained above.

However, it may be said that only an approximate relative value of light energy can be obtained by such simple colorimetric determination of dyestuff produced by light having the same distribution of wave length. And also, at least, the mere estimation of the order of energy may be given. For instance, in the case of measuring the solar ultra-violet light intensity, the following approximate treatment can be allowed.

4. When we combine the wave length distribution curve of the solar radiation with that of the sensitivity of the leuco-base solution, an almost triangular area is obtained whose base extends from 3450 Å to 2850 Å. The wave length which divides this triangle into two equal areas is 3105 Å. Therefore, we may consider that in measuring the intensity of the ultra-violet solar radiation with our method, it may be approximately assumed without committing a great error as the monochromatic ray having the wave length of 3150 Å. When we put in the formulae (2) and (3) the value of ν corresponding to this wave length, the value of κ is obtained as follows:

$$\kappa = 0.03423 \times 10^4 \text{ erg/cm.}^2, \text{ min.}$$

With the above value of κ , we can calculate the intensity of the ultra-violet ray of the sun quite approximately by multiplying E by the reciprocal of the rate of absorption (0.019), assuming that the light energy is fully used for the photochemical decomposition of leuco-base molecules. As stated above, this is not the case, therefore the calculated value would be always smaller than the true intensity. But the relative intensity of the ultra-violet radiation of the sun can be fairly well measured by this method. It has been applied with good results to observe even the rapid change of radiation as in the case of the solar eclipse, or weaker radiation such as on a rainy day. The sensitivity and the convenience of this method are by far better than other chemical methods and comparable even to photo-electrical tubes. But it is a weak point of this method that the sensitivity decreases gradually in the course of time.

Summary

The author has contrived a new instrument to measure the relative intensity of the ultra-violet radiation using the leuco-base of crystal violet. A quartz glass ampule containing the leuco-base solution is exposed to light and the dyestuff thus produced is determined colorimetrically with a series of a standard solution of crystal violet contained in ampules of the same size. The method of measurement is explained.

In conclusion the author expresses his thanks to Dr. Okada, the former director of the Central Meteorological Observatory of Japan for his valuable suggestions on this work.

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Détermination du domaine de la concentration du sel complexe qui précipite la protéine. Les sels complexes cationiques ne peuvent pas toujours précipiter la protéine, tandis que les sels anioniques le font. L'alubumine d'œuf n'est guère précipitée par les sels complexes cationiques, ni la gélatine non plus. En prenant la solution de la caséine à 0.5 % ou celle de l'alubmine à 0,5 %, on les a dissous dans le tampon (pH 8.8 ou 2), et on a ajouté 1cc. de la solution de diverses concentrations du sel complexe à 1 cc de chaque solution. On en a examiné les résultats de précipitation après trente minutes, le résultat est montré dans la table suivante en indiquant # la précipitation parfaite, et ++, + la précipitation imparfaite.

a. *Précipitation de la protéine par les sels complexes cationiques.* Les sels complexes cationiques ne précipitent pas toujours la protéine. Aucune protéine n'est précipitée par les sels complexes du cobalt de la valence +1. Le sel complexe qui n'a pas de charge électrique tel que $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ ne précipite jamais la protéine. Le domaine de la concentration du sel complexe pour la précipitation est montré ci-dessous.

Table 1.

Sel complexe	Caséine	Insuline	Albumine d'œuf	Gélatine
$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	—	—	—	—
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2(\text{SO}_4) \cdot 3\text{H}_2\text{O}$	—	—	—	—
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]_{(6)}^{(1)}\text{Cl}$ (Trans) (Croséo)	—	—	—	—
$[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$ (Purpuréo)	+	+	—	—
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ (Xantho)	+	+	—	—
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$	+	+	—	—
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (Luthéo)	++	++	—	—
$[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	++	++	—	—
$[\text{Co}(\text{NH}_2)_5\text{H}_2\text{O}](\text{NO}_3)_3$ (Roséo)	++	++	—	—
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_3\text{H}_2\text{O}$ (Diroséo)	++	++	—	—
$[\text{Co}(\text{en})_2(\text{NH}_3)_2]_{(6)}^{(1)}\text{Br}_3 \cdot \text{H}_2\text{O}$ (Trans)	++	++	—	—
$\left[(\text{NH}_3)_4\text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co}(\text{NH}_3)_4 \right] \text{Cl}_4 \cdot 4\text{H}_2\text{O}$	++	++	+	—
$\left[\text{en}_2\text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co} \begin{array}{c} \text{H}_2\text{O} \\ \diagup \quad \diagdown \\ \text{H}_2\text{O} \end{array} \text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{en}_2 \right] \text{Cl}_4$	++	++	+	—
$\left[\text{Co} \left(\begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co en}_2 \right)_3 \right] (\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$	##	##	+	—

Table 2.

Sel complexe	Protéine	La concentration pour la précipitation (mol)
$[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$ (Purpuréo)	Caséine	1/60
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$	„	1/60
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ (Xantho)	„	1/40
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (Luthéo)	„	1/20—1/300
$[\text{Co en}_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	„	1/40—1/300
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_2$ (Roséo)	„	1/80—1/250
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (Diroseo)	„	1/40—1/250
$[\text{Co en}_2(\text{NH}_3)_2]^{(1)}_{(6)}\text{Br}_3 \cdot \text{H}_2\text{O}$	„	1/40—1/300
$\left[(\text{NH}_3)_4\text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co}(\text{NH}_3)_4 \right] \text{Cl}_4 \cdot 4\text{H}_2\text{O}$	„	1/100—1/1000
$\left[\text{en}_2\text{Co} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co} \begin{array}{c} \text{H}_2\text{O} \\ \diagup \quad \diagdown \\ \text{H}_2\text{O} \end{array} \text{Co en}_2 \right] \text{Cl}_4$	„	1/100—1/1000
$\left[\text{Co} \left(\begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Co en}_2 \right)_3 \right] \text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$	„	1/100—1/5000

b. *Précipitation de la protéine par les sels complexes anioniques.* Les sels complexes anioniques peuvent parfaitement précipiter la protéine.

Table 3.

Sel complexe	Caséine	Insuline	Albumine d'œuf	Gélatine
$\text{K}[\text{Co}(\text{NH}_3)_2\text{NO}_2)_4]$ (Sel Erdmann)	##	##	##	+
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	##	##	##	+
$\text{K}_3[\text{Co}(\text{CN})_6]$	##	##	##	+

Le domaine de la concentration du sel complexe pour la précipitation est montré ci-dessous.

Table 4.

Sel complexe	Protéine	La concentration pour la précipitation (mol)
$\text{K}[\text{Co}(\text{NH}_3)_2\text{NO}_2)_4]$ (Sel Erdmann)	„	1/60
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	„	1/40—1/300
$\text{K}_3[\text{Co}(\text{CN})_6]$	„	1/100—1/300
$\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ (sel Erdmann)	Albumine d'œuf	1/60
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	„	1/40—1/350
$\text{K}_3[\text{Co}(\text{CN})_6]$	„	1/100—1/300

Calcul de l'équivalent de l'ion complexe combiné avec 1g. de la protéine. La protéine est précipitée par les sels complexes, et on peut séparer par la centrifugation en la lavant cinq fois par l'eau, et on peut la sécher dans l'exsiccateur. En prenant 20-30 mg. de la protéine précipitée et la décomposant par l'acide azotique fumant, on peut colorimétri-

quement faire le dosage du cobalt en utilisant le sel du nitroso-R⁽³⁾. Pour ce dosage du cobalt, on a d'abord calculé la quantité de l'ion complexe combinée avec 1g. de la protéine, et déterminé l'équivalent de son ion complexe.

a. *Equivalents des ions complexes des sels complexes cationiques.* Les équivalents des ions complexes des sels complexes cationiques sont montrés ci-dessous. (pH 8.8)

Table 5.

Sel complexe	Protéine	Concentration du sel complexe (mol)	Co (%)	Ion complexe (%)	Equivalent combiné avec 1g. de la protéine ($\times 10^{-5}$)
[Co(NH ₃) ₅ Cl](NO ₃) ₂ (Purpuréo)	Caséine	1/30	{1.81 1.72	{5.50 5.23	65 62
[Co(NH ₃) ₅ NO ₂]Cl ₂	"	"	{1.54 1.72	{5.38 6.01	55 62
[Co(NH ₃) ₅ NO ₂]Cl ₂ (Xantho)	"	"	{1.71 1.94	{5.51 6.25	61 70
[Co(NH ₃) ₅]Cl ₃ (Luthéo)	"	1/60	{1.47 1.32	{4.01 3.60	78 70
[Co en ₃]Cl ₂ ·3H ₂ O	"	"	{1.51 1.44	{6.12 5.83	82 78
[Co(NH ₃) ₅ H ₂ O](NO ₃) ₃ (Roséo)	"	"	{1.35 1.41	{3.71 3.87	71 75
[Co(NH ₃) ₄ (H ₂ O) ₂](NO ₃) ₃ ·H ₂ O (Diroséo)	"	"	{1.30 1.43	{3.59 3.95	68 76
[Co en ₂ (NH ₃) ₂] ⁽¹⁾ ₍₆₎ Br ₃ ·H ₂ O	"	"	{1.49 1.38	{5.38 4.98	80 74
[(NH ₃) ₄ Co<OH>Co(NH ₃) ₄]Cl ₄ ·4H ₂ O	"	1/150	{2.58 2.39	{6.30 5.83	93 86
[en ₂ Co<OH>Co<OH>Co en ₂]Cl ₄	"	"	{3.49 3.60	{10.23 10.60	88 91
[Co<OH>Co en ₃] ₃ (NO ₃) ₆ ·3H ₂ O	"	5/1125	{3.78 3.91	{11.18 11.56	108 112
"	Albumine d'œuf	1/300	{1.18 1.62	{3.48 4.79	31 43

Quant aux sels complexes cationiques du cobalt, les équivalents ne sont pas déterminés. C'est-à-dire, l'équivalent du $\left[\text{Co} \left(\begin{smallmatrix} \text{OH} \\ \text{Co en}_2 \end{smallmatrix} \right) \right] (\text{NO}_3)_6$ est 108×10^{-5} , et celui du $[\text{Co}(\text{NH}_3)_5]\text{Cl}_3$ est 78×10^{-5} , et celui du $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$ est 65×10^{-5} . Quant aux sels complexes de la valence +2, si on répète la précipitation dans les mêmes conditions, les équivalents des ions complexes ne s'accordent pas et donnent des différences assez grandes. (plus de 10 %).

(3) H. S. van Klooster, *J. Am. Chem. Soc.*, 43 (1921), 746; F. J. Stare et C. A. Elvehjem, *J. Biol. Chem.*, 99 (1933), 473; H. T. Macpherson et J. Stewart, *Biochem. J.*, 32 (1938), 763; N. Tanaka, *ce bulletin*, 18 (1943), 436.

b. *Équivalents des ions complexes des sels complexes anioniques.* Les équivalents des ions complexes des sels complexes anioniques sont montrés ci-dessous.

Table 6.

Sel complexe	Protéine	Concentration du sel com- plexe	Co (%)	Ion complexe (%)	Equivalent combiné avec 1g. de la pro- téine ($\times 10^{-5}$)
$K[Co(NH_3)_2(NO_2)_4]$ (Sel Erdmann)	Caséine	1/25	4.44	20.85	95
$Na_3[Co(NO_2)_6]$	„	1/40	{1.61 1.58	{9.14 8.97	{90 88
$K_3[Co(CN)_6]$	„	„	1.72	6.27	93
$K[Co(NH_3)_2(NO_2)_4]$ (Sel Erdmann)	Albumine d'œuf	1/25	{3.50 3.55	{16.43 16.67	{71 72
$Na_3[Co(NO_2)_6]$	„	1/40	{1.31 1.35	{7.44 7.67	{72 74
$K_3[Co(CN)_6]$	„	„	1.45	5.29	78

Quant aux sels complexes anioniques du cobalt, les équivalents restent constants. C'est-à-dire, l'équivalent du $K[Co(NH_3)_2(NO_2)_4]$ est 95×10^{-5} (caséine), et celui du $Na_3[Co(NO_2)_6]$ est 90×10^{-5} (caséine).

Conclusion 1. Comme S. E. Michael, j'ai classé tous les sels complexes cobaltiques en complexe cationique et complexe anionique. Le premier précipite la protéine dans le domaine alcalin du point isoélectrique et le second précipite dans le domaine acide.

2. Le sel complexe qui n'a pas de charge électrique tel que $[Co(NH_3)_3(NO_2)_3]$ ne précipite jamais la protéine.

3. Les sels complexes cationiques de cobalt ne précipitent pas toujours la protéine.

4. La précipitation de la protéine par les sels complexes cationiques du cobalt est imparfaite, et les complexes cobaltiques de la valence +1, tels que $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$, $[Co(NH_3)_4(NO_2)_2]Cl$ ne peuvent pas précipiter la protéine.

5. On peut cependant parfaitement précipiter la protéine par les complexes anioniques du cobalt.

6. Quant aux sels complexes cationiques du cobalt qui ne peuvent pas montrer la précipitation parfaite de la protéine, les équivalents ne sont pas déterminés. A la même valence, ses équivalents sont approximativement identiques, tandis qu'en valence différente, ils ne sont pas identiques et diminuent proportionnellement à la valence.

7. Quant aux sels complexes anioniques du cobalt, la précipitation est parfaite, et les équivalents combinés avec 1g. de la protéine restent constants indépendamment de la valence.

8. Les équivalents des ions complexes cationiques du cobalt combinés avec 1g. de l'albumine d'œuf sont très petits.

9. De ces résultats, on peut conclure que la protéine et le sel complexe peuvent réagir stoichiométriquement, mais la précipitation de la

protéine par les sels complexes cationiques du cobalt n'est pas parfaite, et son équivalent de l'ion complexe combiné avec 1 g. de la protéine ne montre pas d'équivalent maximum. On peut cependant obtenir la précipitation parfaite par les sels complexes anioniques du cobalt, et son équivalent montre l'équivalent maximum.

En terminant ce compte rendu de mes recherches, j'ai à exprimer mes sincères remerciements à M. le Prof. Kénjiro Kimura pour les aimables et très utiles indications, ainsi qu'à M. M les Profs. Toshi Inoué, Taku Uémura, et Eiji Ochiai qui ont bien voulu me prêter leur bienveillant concours dans mes expériences.

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Études spectroscopiques des complexes métalliques du diphénylthiocarbazone. I⁽¹⁾.

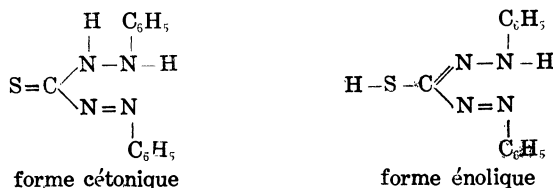
Par Taku UÉMURA et Seinosuke MIYAKAWA.

(Reçu le 19 janvier, 1949.)

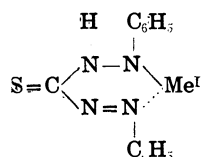
Introduction. Le diphénylthiocarbazone (dithizone) donne plusieurs complexes intermoléculaires métalliques qui sont généralement solubles dans le chloroforme ou le tétrachlorure de carbone en donnant des solutions colorées foncées. On peut donc utiliser cette réaction à l'analyse qualitative et quantitative⁽²⁾. H. Fischer⁽²⁾ a déjà avancé une proposition sur l'existence de deux tautomères pour ces complexes, parce que le dithizone montre deux sortes de constitutions : soit cétonique, soit énolique, qui alternent comme ci-dessous

(1) Exposé fait lors de la 1^{ère} Séance annuelle de la Société chimique du Japon, le 4 avril, 1948.

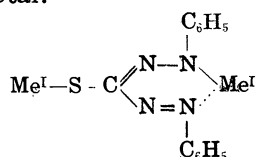
(2) H. Fisher, *Z. angew. Chem.*, 47 (1934), 685.



Le composé cétonique stabilisé dans la solution acide ou neutre, prend la forme de



tandis que le composé énolique qui est stable dans la solution alcaline prend la constitution de laquelle deux atomes d'hydrogène peuvent être substitués par le même métal.



Plusieurs études sur la microanalyse des métaux en utilisant le dithizone⁽³⁾, ont été déjà faites, mais les recherches spectrochimiques sur les complexes du dithizone n'étaient analytiquement poursuivies que dans la région visible⁽⁴⁾. Nous avons quantitativement mesuré les spectres d'absorption du dithizone et certains de ses complexes dans la région visible et ultraviolette.

Procédé expérimental. Comme le dithizone est très oxydable et qu'on peut l'obtenir au marché et qu'il est presque toujours trouvé dans ses produits oxydés, il est nécessaire de le purifier et en préparer la solution type. On dissout d'abord 20 mg. du dithizone dans 100 c.c. du tétrachlorure de carbone, puis on filtre la solution, puis on ajoute 100 c.c. d'ammoniaque de 0,2 normal et remue ce mélange. En séparant la couche du dissolvant, on y ajoute à nouveau 100 c.c. du tétrachlorure de carbone, et on acidifie le mélange par l'acide chlorhydrique. A ce moment, le dithizone se transmet de la couche aqueuse à celle du tétrachlorure de carbone. Cette solution est séparée et lavée plusieurs fois par l'eau, puis passée au filtre en papier sec pour la conserver à l'abri de la lumière. Pour déterminer la concentration du dithizone, on titre 0,01 normal de la solution d'argent nitrate par la solution du dithizone. La solution dont la concentration a été déterminée est utilisée pour mesurer ses spectres d'absorption en la diluant convenablement. L'eau, le tétrachlorure de carbone, l'ammoniaque et l'acide chlorhydrique qui sont employés pour ces expériences, sont deux fois distillés

(3) Voir les bibliographies qui se trouvent dans "Organic Reagents in Inorganic Analysis", par I. Mellan (1941), p. 96.

(4) H. A. Liebhafsky et E. H. Winslow, *J. Am. Chem. Soc.*, **59** (1937), 1966; H. Fischer et W. Weyle, *Wiss. Veröff. Siemens-Werk*, **14**, II (1935), 41.

pour éviter toutes impuretés qui pourraient être des causes d'erreur. Dans ces présentes études, les concentrations du dithizone et des complexes dans le tétrachlorure de carbone ou dans l'ammoniaque restent entre 2×10^{-5} et 4×10^{-5} mol/l. Nous nous sommes servis du spectrographe en quartz "type E 2" construit par Hilger et du spectrophotomètre Spekker construit par Shimazu pour la région ultraviolette. Le spectrophotomètre Nutting construit par Hilger a aussi été utilisé pour la région

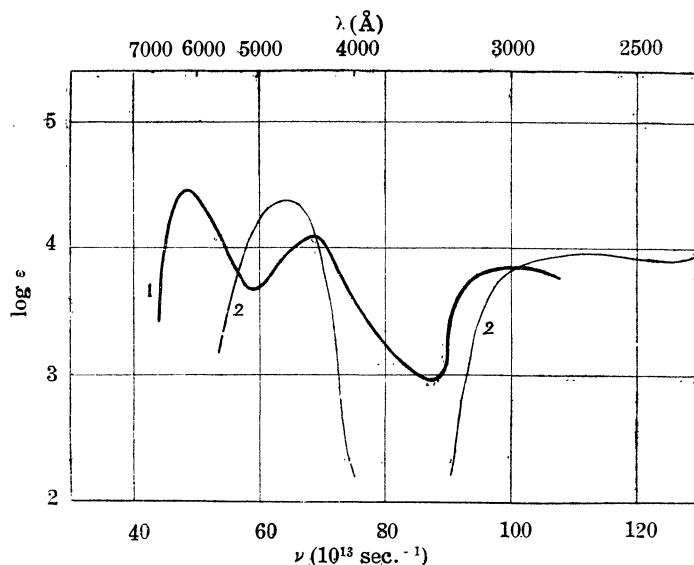


Fig. 1. Absorption du dithizone.

1. Forme cétonique (solution du tétrachlorure de carbone).
2. Forme énolique (solution ammoniacale de 0.2 normal).

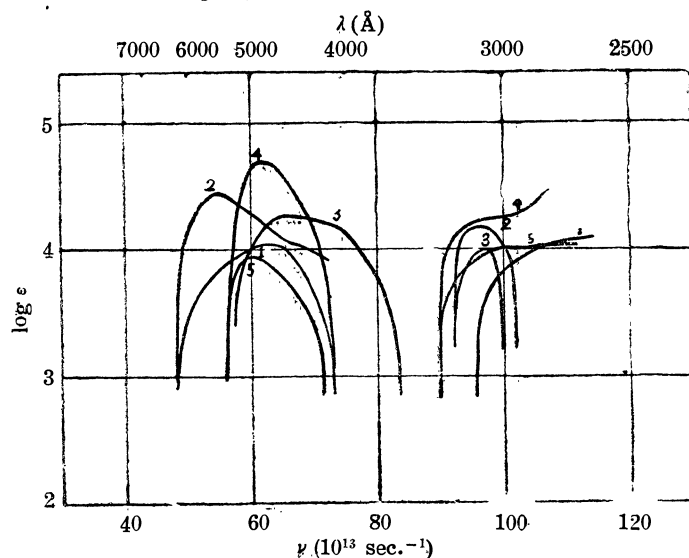


Fig. 2. Absorption des complexes.

1. AgD, 2. CuD₂, 3. CuD, 4. HgD₂, 5. HgD.
(solution du tétrachlorure de carbone).

visible. Les résultats sont indiqués dans la table suivante et par les figures 1, 2 et 3.

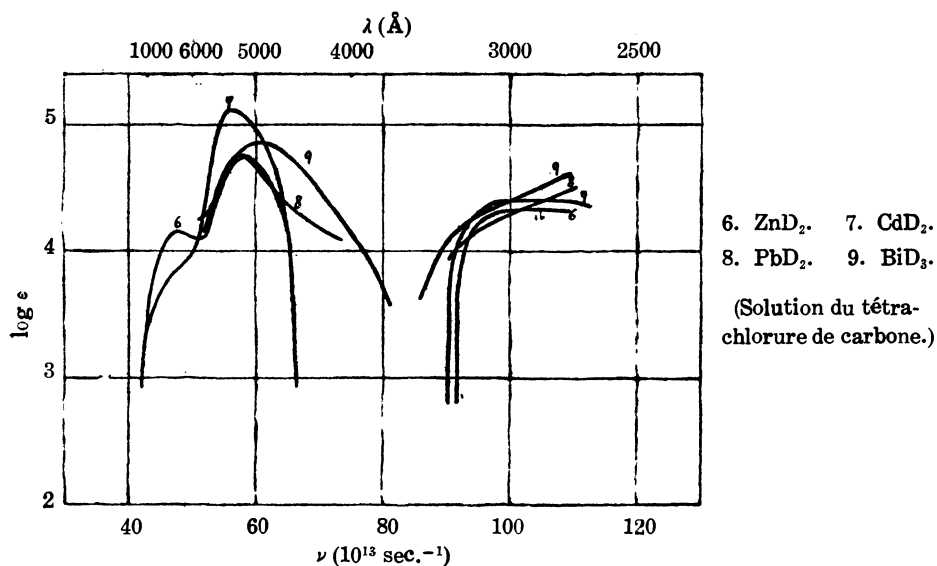


Fig. 3. Absorption des complexes.

Table. Absorption lumineuse par le dithizone et ses complexes métalliques.

ϵ = valeurs des coefficients d'absorption moléculaire.

D = dithizone. λ = longueur d'onde. ν = fréquence.

Formes des composés	λ	ν	ϵ
D (cétonique)	620 m μ	51,0.10 ⁻¹³ sec. ⁻¹	3,05.10 ⁻⁴
	440	68,1	1,26
	300	100	0,71
D (énolique)	465	64,5	2,4
	265	113,0	0,96
AgD	480	62,5	1,18
CuD_2	555	54,0	2,84
	310	96,7	1,52
CuD	455	65,9	0,92
	308	97,3	0,50
HgD_2	483	62,0	5,32
	310	96,7	1,66
HgD	500	60,0	0,95
	300	100,0	1,00
ZnD_2	635	47,2	1,52
	520	57,6	5,76
	280	107,0	2,10
CdD_2	540	55,5	12,20
	285	105,5	2,52
PbD_2	522	57,5	5,64
BiD_3	490	61,2	7,17

Spectres d'absorption. (A) *Dithizone*. Le dithizone de la forme cétonique dissous dans le tétrachlorure de carbone donne trois bandes d'absorption dont les longueurs d'onde sont respectivement chaque pouvoir absorbant maximum aux $620\text{ m}\mu$, $440\text{ m}\mu$ et $300\text{ m}\mu$. Nous les appelons la première, deuxième et troisième bande d'absorption d'après la longueur d'onde. La forme énolique du dithizone peut être obtenue en ajoutant 0,2 normal d'ammoniaque au même volume de sa solution du tétrachlorure de carbone et en remuant ces mélanges. Le dithizone se transmet complètement à la couche aqueuse par ce traitement et se change en forme énolique. Dans ce cas, pour mesurer l'absorption lumineuse, on met 0,2 normal d'ammoniaque dans le contenant du dissolvant pour compenser l'absorption du dissolvant. La forme énolique donne une bande claire à $465\text{ m}\mu$ dans la région visible, et une bande vague à $265\text{ m}\mu$ environ dans la région ultraviolette.

(B) *Complexes métalliques du dithizone*. Suivant H. Fischer⁽²⁾ nous avons préparé les solutions de certains complexes dissous dans le tétrachlorure de carbone par les réactions entre le dithizone en solution du tétrachlorure de carbone et des sels métalliques en solution aqueuse.

(1) AgD : Ce sel peut être obtenue comme la forme cétonique de sa solution acide. Sa solution du tétrachlorure de carbone est jaune, et montre une bande d'absorption à $480\text{ m}\mu$, perdant la première et la deuxième bande de la forme cétonique du dithizone. Son absorption est semblable à celle donnée par la forme cétonique du dithizone lui-même dans la région ultraviolette, mais nous ne sommes pas capables de mesurer la longueur d'onde du côté plus court, parce qu'elle est couverte par l'absorption du tétrachlorure de carbone lui-même.

(2) CuD_2 : La solution du tétrachlorure de carbone de la forme cétonique a été préparé de la solution acide du sel cuivrique en montrant la couleur violette et une bande à $555\text{ m}\mu$. Elle présente encore une bande distincte à $310\text{ m}\mu$ qui est correspondante à la troisième bande de la forme cétonique du dithizone.

(3) CuD : La forme énolique obtenue de la solution aqueuse neutre du sel cuivrique et la solution du tétrachlorure de carbone est brune. Cette solution présente deux bandes d'absorption à $455\text{ m}\mu$ et $308\text{ m}\mu$. La première est plus hypsochromique que celle de CuD_2 . La raison de ce phénomène nous semble être dans la constitution du radical thiocarbonyle $\text{S} = \text{C} <$ qui devrait peut-être changer en $-\text{S}-\text{C} \ll$.

(4) HgD_2 : La solution acide du sel mercurique où se trouve comme la forme cétonique est jaune-orange, et montre une bande à $483\text{ m}\mu$ dans la région visible et une autre à $310\text{ m}\mu$ environ dans la région ultraviolette.

(5) HgD : C'est la forme énolique préparée de la solution neutre qui donne la couleur rouge et le pouvoir absorbant maximum à $500\text{ m}\mu$.

La position de cette bande est influencée et plus bathochromique que celle de HgD_2 , mais l'absorption ultraviolette est semblable à celle de HgD_2 .

(6) ZnD_2 : La forme cétonique peut être obtenue de la solution acide. La couleur de cette solution est rouge-violette et donne deux bandes dans la région visible qui présentent respectivement leur maxima à $635 \text{ m}\mu$ et $520 \text{ m}\mu$. La première bande coïncide à la position de celle de la forme cétonique du dithizone. On ne peut pas exactement juger si ce résultat est dû à l'absorption du dithizone lui-même donnée par la décomposition du complexe ou dû à une nouvelle absorption spécialement produite.

(7) CdD_2 : La solution faiblement alcalisée de ce composé donne sa forme cétonique. Cette solution est rouge et montre une bande ayant le pouvoir fortement absorbant. Cette bande se trouve à $540 \text{ m}\mu$, mais elle n'est pas distincte comme celle présentée par ZnD_2 .

(8) PbD_2 : La solution rouge de la forme cétonique montre une bande à $552 \text{ m}\mu$. On ne pouvait trouver nulle absorption maximum jusqu'à $270 \text{ m}\mu$ dans la région ultraviolette, et c'est encore difficile de la mesurer dans cette région par la bande d'absorption du dissolvant tétrachlorure de carbone.

(9) BiD_3 : La forme cétonique orange qui possède trois molécules du dithizone peut être obtenue de la solution neutre. Cette solution donne une bande large à $490 \text{ m}\mu$ dans la région visible. On ne peut cependant trouver l'absorption maximum dans le domaine ultraviolet comme dans le cas de PbD_2 .

Résumé.

(1) Nous avons mesuré les absorptions lumineuses en région visible et ultraviolette du dithizone et ses complexes métalliques (Ag, Cu, Hg, Zn, Cd, Pb et Bi) dans leurs solutions du tétrachlorure de carbone.

(2) Les bandes d'adsorption de ces complexes métalliques donnent généralement deux bandes en région visible et ultraviolette. La première en région visible change sa position du pouvoir absorbant maximum suivant la sorte de métaux combinés, mais la longueur d'onde d'absorption du pouvoir maximum de la deuxième bande est à peu près invariable et grossièrement coïncide à celle du dithizone, lors même que les métaux combinés changent.

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Actinomycin J₂, a By-product from a Strain of Actinomyces.

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An antibiotic (activity; 1:10,000,000 against *staphylococcus aureus* Terajima) has been obtained from *actinomyces flavus*,⁽¹⁾ which seems to be related to actinomycin A of Waksman⁽²⁾, but considering the fact that the position of the absorption maximum in 95 % alcohol is 435 mμ, compared with the values 450 mμ and 230~250 mμ obtained by Waksman. and that there is a difference in the percentage of carbon (author: 55.45 %, Waksman: 59.01 %), it is suggested that this substance is not quite identical with actinomycin A. Thus we shall call this substance actinomycin J₁. Meanwhile, another antibiotic, with a minor activity (1:160,000) seemed to have been extracted from the same strain, corresponding to actinomycin B of Waksman. We have studied its chemical structure and finally come to the conclusion of its being the dodecyl ester of 5-keto-stearic acid:



by means of synthesis. Though this synthesized sample was identical with the natural specimen, it demonstrated no activity. Therefore, it must be concluded that the activity must have been due to a minute amount of the former actinomycin J₁ existing as an impurity in the second substance.

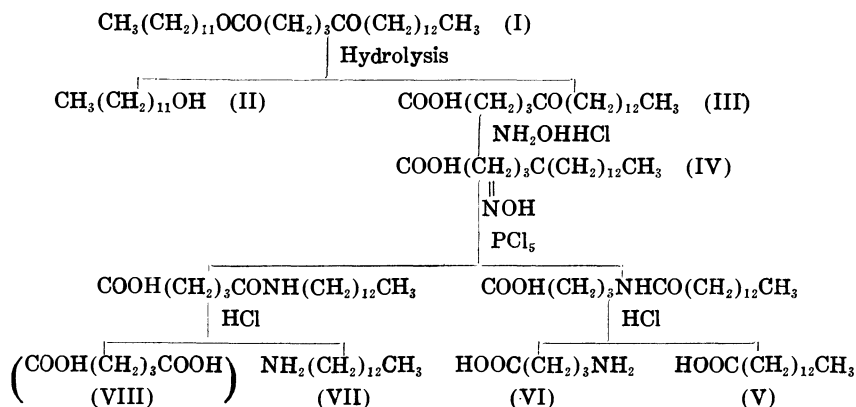
This second substance may be named actinomycin J₂ for convenience, notwithstanding its inactivity, and the experimental data for the determination of its chemical structure and synthesis are here reported.

Actinomyces flavus was cultivated on a Czapeck-Dox solution, extracted after two weeks and crystallized from methanol (m. p. 59–61°C).

It possesses a waxlike nature and odor, dissolving in all the wax-dissolving solvents. The fact that the ultra-violet absorption spectra showed no selective absorption suggested that it was probably a simple aliphatic compound containing none of the specific groups. The tetra-nitromethane and bromine tests were negative, thus excluding the presence of a double bond. Analysis gave the formula C₃₀H₅₈O₃(I), and by the action of ethanolic potassium hydroxide, the original substance was hydrolysed into two fractions, C₁₂H₂₆O (II) and C₁₈A₃₆O₃ (III). (Scheme I)

(1) Y. Hirata and K. Nakanishi, *J. Penicillin*, 2 (1949), 180.

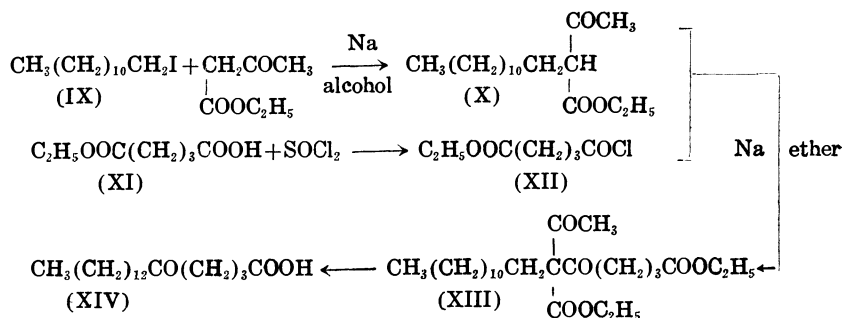
(2) S. A. Waksman and H. B. Woodruff, *J. Bact.*, 40 (1940), 583; *J. Biol. Chem.*, 142 (1942), 519.



Bubbles which were generated by the action of sodium bicarbonate showed (III) to be an acid, while the negative results obtained from an effort to esterify the substance by means of *p*-nitrobenzoyl chloride and to dehydroxylize it by reduction with hydroiodic acid in a sealed tube, indicated that (III) was not a hydroxy acid. On the other hand, such derivatives as the 2,4-dinitrophenyl hydrazone and the oxime (IV) showed it to be a keto acid. The oxime was submitted to the Beckmann rearrangement and after hydrolysis with hydrochloric acid, (V) (VI) and a minute amount of (VII) were obtained, thus suggesting its structure to be 5-keto-stearic acid. (VII) could not be identified.

The melting point of (II) (22°) and the α -naphthyl urethane (80°) corresponded with that of dodecyl alcohol. Therefore, the structure of J₂ was established to be the dodecyl ester of 5-keto-stearic acid and this was further proved by synthesizing the substance and mixing it with the natural specimen, upon which no depression of melting point was observed. The synthesis was carried out by two methods, of which the latter gave a considerable yield (42 %).

The first method, analogous to that employed by Robinson and Robinson⁽³⁾ (scheme II) is concluded by gradual hydrolysis under three steps of Scheme II. First Method.



(3) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 127 (1925), 175.

modified Czapeck-Dox medium (NaNO_3 6 g., K_2HPO_4 2 g., KCl 1 g., $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 1 g., $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.02 g., glucose 60 g., peptone 10 g., distilled water 1000 c.c.) at 27°C for two weeks and shaken occasionally.

The culture liquid became brown-black and the floating bodies gradually acquired a yellowish color.

Extraction. The body and culture liquid were separated and the former extracted with acetone. The latter was shaken with clay and adsorbed, extracted with acetone, and the combined acetone solutions evaporated by submitting to a flash evaporator. The resulting orange yellowish turbid aqueous solution was extracted with ether, and red plates (actinomycin J_1) were obtained by concentrating the ether solution. After removing the crystals by decantation the concentration was repeated, upon which a second crop of J_1 precipitated. J_2 was obtained from the residue as white wax-like plates using methanol or ethanol as recrystallization solvent. Yields were 150 mg./l. and 80 mg./l. for J_1 and J_2 respectively. Melting point of J_2 : $59-61^\circ$.

(Found: C, 76.36; H, 12.44. Calculated for $\text{C}_{30}\text{H}_{58}\text{O}_3$: C, 77.2; H, 12.5%). Molecular weight determined by the Rast method gave 455. Calculated: 463.

Ultra-violet absorption spectra. The 0.1%, 0.01%, and 0.001% solutions in 96.5% alcohol showed no selective absorption. the absorption of a 100 mm. solution beginning from $310\text{ m}\mu$.

Hydrolysis. Hydrolysis of J_2 was carried out by the action of 4% alcoholic KOH on the sample (185 mg.) at room temperature for three days.

The alcohol was evaporated on a steam-bath and after addition of water to the residue, submitted to steam distillation, upon which (II) came over into the distillate as white crystals, possessing an odor of higher alcohol. The residue was acidified, extracted with ether, the ether evaporated and the residue (III) recrystallized from ethyl alcohol. m. p.: 81° . Found: C, 71.82; H, 13.05. Calculated for $\text{C}_{18}\text{H}_{36}\text{O}_3$: C, 72.0; H, 12.0%.

Dodecyl alcohol (II). M. p. 22° , alone or mixed with dodecyl alcohol. α -Naphthyl urethane: m. p. 79° (ligroin).

p-Bromophenacyl ester of 5-keto-stearic acid. 1N NaOH was titrated to an alcoholic solution of the sample (25 mg.), using phenolphthalein as indicator. The solution should be kept slightly acidic and the concentration of alcohol kept above 70%. One to two per cent. less than the equivalent amount of p-Bromophenacyl bromide is added to this solution, boiled on the bath under reflux for 1 hour, the flask cooled, water added and the separated solid recrystallized from dilute alcohol. m. p. 105° (uncorr.).

2,4-Dinitrophenyl hydrazone of 5-ketostearic acid. The alcohol and sulfuric acid solution of 2,4-dinitrophenyl hydrazine was added to the alcoholic solution of the keto acid and left overnight in the ice-box. After removing the red crystals of 2,4-dinitrophenyl hydrazine sulfate which may occur, the remaining red oil crystallized after 1-2 days. M. p. 110° (uncorr.).

5-Ketostearic acid oxime (IV). A mixture of the keto acid (70 mg.), anhydrous pyridine (1.3 c.c.) and hydroxyl amine hydrochloride (30 mg.) (molecular ratio; 1:1:3) was gently boiled for 3 hours under reflux, poured into water and acidified with HCl. The resulting oxime was extracted with ether, and crystallized from alcohol. This method using pyridine enabled the oxime to be prepared more easily and completely than the usual method with alcoholic KOH. m. p. 64° . Found: N, 4.90. Calculated for $\text{C}_{18}\text{H}_{37}\text{O}_3\text{N}$: N, 4.4%.

Beckmann rearrangement and hydrolysis of the oxime (IV). PCl_5 was added under cooling with an ice-mixture to the dilute ether solution of the oxime obtained above and kept overnight at 0° . A sufficient amount of PCl_5 should be added to retain a precipitate of PCl_5 . The mixture is shaken with ice-water, the ether evaporated after drying over K_2CO_3 and the residue heated eight hours with conc. HCl at 160° in a sealed tube.

Myristic acid (V). Water is poured into the reaction mixture and the white crystals

extracted with ether. M. p. 53° (alcohol), alone or mixed with myristic acid. Found: C, 72.58; H, 12.01. Calculated for C₁₄H₂₈O₂: C, 73.7; H, 12.3%.

n-Tridecyl amine (VII). The acidic solution was made alkaline, extracted with ether and dry HCl gas passed through, upon which a small amount of fine white needles were obtained. Hygroscopic, decomposed at 100°. Pt-salt (2C₁₃H₂₇N + 2HCl + PtCl₄): 230° (decomp.).

Glutaric acid (VIII). This was unobtainable owing to the minute amount of sample used.

γ-Aminobutyric acid (VI). The alkaline residue was acidified with HCl, evaporated on the water-bath, separated from NaCl by washing with absolute alcohol and the alcohol evaporated. The remaining syrup crystallized into hygroscopic needles when kept in an ice-box. The Pt-salt was obtained and analysed. Found: Pt, 31.02; Calculated for 2NH₂(CH₂)₃COOH + 2HCl + PtCl₄: Pt. 31.88%.

Dodecyl-acetoacetic acid ethyl ester (X). Dodecyl iodide (IX) was prepared by passing HI gas (2.5 mol) through dodecanol (55 g., 0.3 mol) at room temperature, and after washing with water and dilute KOH, distilled; the portions 165–170°/20 mm. collected (40 g.).

16 g. of an oil, b. p. 205°/255 mm., were obtained according to the usual method, employing Na (2.1 g.), ethyl acetoacetate (17.7 g.), absolute alcohol (30 c.c.), n-dodecyl iodide (28 g.): the time of reaction was 5 hours.

4-Carbethoxybutyryl chloride (XII). Monoethyl glutarate (XI) was prepared by a method analogous to that employed by Grün and Wirth⁽⁷⁾ in the semihydrolysis of diethyl sebacate; namely, diethyl glutarate (8 g.) was dissolved in half its volume of absolute alcohol and to this boiling solution a calculated amount of 2N KOH alcoholic solution was added under vigorous stirring. The resulting white mass was poured into a considerable amount of ice-water, and the alcohol removed by distillation under reduced pressure. After extracting the unchanged diester completely with ether, the residue was acidified and extracted with ether. A crude product of the monoester was obtained by evaporating the ether. The ether extract was dried over Na₂SO₄ and distilled. 3 g. of an oil, 143°/7 mm. was obtained. Monoethyl glutarate (1.8 g.) was heated gently on the water bath with thionyl chloride (6 g.) for 3 hours, the excess thionyl chloride removed completely by distillation under reduced pressure and by keeping the residue in vacuum. A high temperature should be avoided throughout all the processes, owing to the instability of the monoester. The chloride (XII) thus obtained was directly submitted to further procedures.

5-Ketostearic acid (XVI) (First method). Na (0.28 g.) was granulated under toluene, washed with ether, suspended in ether (20 c.c.) and (X) gradually added, the clear solution of the sodio derivative being completed by heating on the bath for several minutes. To this solution, 4-carbethoxy-butyl chloride (XIII) dissolved in ether (3 c.c.) was added at 0°; after remaining 30 minutes at room temperature, the mixture was boiled under reflux for 15 minutes, cooled, washed with water and the ether evaporated. The residue was agitated for 8 hours with 5% NaOH (75 c.c.), acidified with acetic acid and collected by means of ether. The product was next boiled with 5% H₂SO₄ (100 c.c.) for 8 hours and steam-distilled in order to remove the methyl tridecyl ketone. The hydrolysis was completed by boiling with 5% NaOH (400 c.c.) for 5 hours. The product crystallized from light petroleum ether (b. p. 40–80°) and methyl alcohol, but the yield was poor, m. p. 81.5°, alone or mixed with the natural keto acid.

Diethyl α-acetoglutarate (XVI). Ethyl 3-bromopropionate (XV) (11.4 g.) ("Organic

(7) A. Grün and T. Wirth, *Ber.*, 55 (1922), 2207.

Synthesis" Coll. Vol. I, p. 263) Na (2.6 g.), absolute alcohol (57 c.c.) and ethylacetoacetate (14.8 g.) were submitted to the usual method, the time of reaction being 5 hours. 2.8 g. of an oil, 153-162°/15 mm. were obtained.

5-Ketostearic acid (Second method) (XIX). Na (0.3 g.) was granulated under toluene, washed with ether, suspended in ether (30 c.c.), and diethyl α -acetoglutarate (XVI) (2.8 g.) gradually added (30 minutes) upon which the sodio-derivative was produced as a white powder. After the addition of myristic acid chloride (XVII) (3 g.), the mixture was left overnight to complete the precipitation of NaCl, boiled under reflux for 20 minutes, washed with water, the ether evaporated and the residue agitated with 3% NaOH (170 c.c.) for 9 hours. The solution was concentrated for one hour on the bath, upon which the crude Na-salt of the keto acid formed a gelatinous mass. The free acid, prepared by the treatment with HCl and extraction with ether, was crystallized from light petroleum ether (b. p. 40-80°) and methyl alcohol. M. p. 81°, alone or mixed with the natural specimen. Yield: 1.5 g. or 42%.

Actinomycin J₂. 5-Ketostearic acid (350 mg.) was converted into its chloride by the action of thionyl chloride at 50°, the excess reagent being removed by reduced pressure. A solution of dodecyl alcohol (250 mg.) in pyridine (3 c.c.) was added to the chloride, heated at 50° for 5 minutes, left overnight at room temperature, poured into water and extracted with ether. The ethereal solution was washed with dil. H₂SO₄ and water, the ether evaporated and the residue dissolved in hot alcohol. The plates which appeared on cooling seemed to be a mixture of dodecyl alcohol and the keto acid. After removing this portion, the ester was obtained by concentrating the remaining alcoholic solution. M. p. 60°, alone or mixed with the natural substance.

Summary.

The constitution of actinomycin J₂ obtained from *actinomyces flavus* has been studied and identified to be the dodecyl ester of 5-ketostearic acid by means of hydrolysis of the original substance, followed by the Beckmann rearrangement and hydrolysis of the oxime of 5-ketostearic acid into myristic acid, γ -aminobutyric acid and a small amount of *n*-tridecyl-amine. Next, the 5-ketostearic acid was synthesized according to two methods, which were concluded respectively by the hydrolysis of condensation products of the type: $\text{CH}_3(\text{CH}_2)_m\text{C}(\text{COCH}_3)(\text{COOC}_2\text{H}_5)\text{CO}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$ and $\text{CH}_3(\text{CH}_2)_{n+1}\text{CO}(\text{COCH}_3)(\text{COOC}_2\text{H}_5)(\text{CH}_2)_{n-1}\text{COOC}_2\text{H}_5$, of which the latter gave a considerable yield, while that of the former was very poor owing to the undesired direction of hydrolysis. The condensation products of 5-ketostearic acid chloride and dodecyl alcohol showed no depression of melting point when mixed with actinomycin J₂, thus proving the constitution of actinomycin J₂ to be the dodecyl ester of 5-ketostearic acid.

These experiments were begun since it seemed that actinomycin J₂ was an antibiotic, but considering the fact that the synthesized specimen demonstrated no such activity, it must be concluded that the original activity was probably due to a minute amount of actinomycin J₁ existing as an impurity, and that actinomycin J₂ is a mere by-product.

In conclusion, the authors wish to acknowledge their indebtedness to

Profs., F. Egami, K. Yamazaki, W. Kimura, H. Umezawa and Ass. Prof. H. Kubo for their kind encouragements and valuable advices given in the course of this study.

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On the Catalytic Decomposition of Carbon Monoxide by Iron.

By Hideo AKAMATU and Kazutoshi SATÔ.

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Introduction. It is known that carbon monoxide is decomposed catalytically by iron or the other transition metals, and free carbon is formed. Studies on this phenomenon were carried out on the standpoint of chemical kinetics by some investigators⁽¹⁾. It was also pointed out by U. Hofmann⁽²⁾ and T. Watanabe⁽³⁾ that the free carbon formed by the decomposition of carbon monoxide on iron surface has graphitelike properties. Commonly, carbons are amorphous, as soot or carbon black, when they are formed by thermal decomposition of carbon compounds. In order to graphitize them, it is necessary to heat them again over the temperature of 2500°C at least. If carbon which is formed by the catalytic decomposition of carbon monoxide at comparatively low temperature such as 500°C, is already graphitized, there must be some special reason for this graphitization.

To find the mechanism of this reaction, we investigated the changes of the structure of iron surface (catalyser) at some intermediate stages of the reaction by the method of electron diffraction.

Experimental and Results. The experimental procedure was not much different from those which had been used by former investigators. Carbon monoxide, produced by the reaction with formic acid and concentrated

(1) H. A. Bahr, *Ber.*, **61** (1928), 2177; **63** (1930), 2226; H. A. Bahr and V. Jessen, *Ber.*, **66** (1933), 1238; U. Hofmann, *Ber.*, **61** (1928), 1180; U. Hofmann and E. Groll, *Z. anorg. allgem. Chem.*, **191** (1939), 414; U. Hofmann and D. W. Münster, *Z. Elektrochem.*, **42** (1936), 504; H. Tsuchiya, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **8** (1929), 206, 609; **10** (1931), 556, 951; S. Horiba and Taikēi Rī, *Rev. Phys. Chem. (Japan)*, **2** (1928), 11; **4** (1930), 73; **5** (1931), 41; F. Olmer, *J. Phys. Chem.*, **46** (1942), 405.

(2) U. Hofmann, *Ber.*, **61** (1928), 1180.

(3) T. Watanabe, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **7** (1928), 1077; **8** (1929), 288.

sulphuric acid, was flowed into the reaction tube from the reservoir after passing through a dryer such as concentrated sulphuric acid and phosphoric anhydride. For the reason which will be described in the latter section, attention was paid to remove the trace of oxygen in the reaction gas. For this purpose, the gas was passed through the basic solution of potassium pyrogallate and then the heated copper gauze.

The reaction tube was a quartz tube, a part of which could be heated by an electric furnace. The furnace was a small type one, of which length was about 20 cm., and could be slid along the reaction tube. To take out the catalyser from the reaction tube at a certain stage of the reaction, the electric furnace was slid off and the tube could be quickly cooled.

A piece of iron, Kahlbaum's electrolytic iron, was used as catalyser. For the investigation by the electron diffraction method, the surface of the catalyser was polished to flatness by emery paper. To set the catalyser in the reaction tube, a porcelain boat was used.

The gas flowing out from the reaction tube was exhausted after passing through the baryta solution. This solution will be turbid with carbon dioxide when the reaction proceeds as $2\text{CO} \rightarrow \text{C} + \text{CO}_2$.

It took commonly 5~10 hours till the decomposition began to proceed, under the condition in which the reaction temperature was 500°C , and the flowing velocity of carbon monoxide was 400 c.c. per hour. Once the reaction began to proceed, however, the decomposition took place smoothly and free carbon would be formed gradually on the surface of the catalyser.

The electron diffraction patterns of the surface of the catalyser were taken at two intermediate stages of the reaction. The first was when the decomposition had just begun to proceed, that was after a short time when the turbidness of the baryta solution by CO_2 had begun to take place. At this stage, free carbon was not yet found on the catalyser, while the iron surface had lost metallic lustre and become opaque. The observed values of the electron diffraction pattern are shown in Table 1. It is quite different from the pattern of pure iron. It was proved that this pattern belongs to that of cementite. In Table 1, the x-ray diffraction data of cementite⁽⁴⁾ are also shown. Both spacings observed by x-ray and electron diffraction coincide satisfactorily with each other. From this result, it was found that at the first stage of the reaction cementite had been formed on the surface of iron catalyser.

The second electron diffraction pattern was taken when further decomposition had proceeded (after 15 hours from the beginning). At this stage, the surface of the catalyser was changed to black or blacky

(4) The X-ray data of cementite are taken from the values observed by A. Ôsawa and S. Takeda, *Kinzoku no Kenkyu*, 8 (1931), 181.

Table 1.

The electron diffraction pattern of the surface of the ironcatalyser at the first stage of the reaction. (Cementite).

Values of Spacings observed by Electron Diffraction		Corresponding x-ray Data for Cementite.	
2.10 Å	w.	2.10 Å	m. (210)
2.025	m.	2.01	v.s. (211), (103)
1.86	m.	1.855	v.s. (122), (113)
1.685	w.	1.675	m. (023)
1.59	w.	1.58	m. (123), (014)
1.51	w.	1.50	m. (301)
1.36	v.w.	1.36	m. (302), (320)
1.21	v.w.	1.21	v.s. (141)
1.155	w.	1.155	v.s. (142), (400)
1.125	m. diffuse.	1.121	v.v.s. (240)
0.912	w.		
0.795	m.		

grey color in parts, but carbon had not yet been separated in powder form. The spacings observed from this pattern are shown in Table 2. It consists of the carbon pattern principally, but some spacings belonging to cementite are also found. The latter were weak. By using the shorter wave of the cathod-ray, however, the reflected rings belonging to cementite could be made strong to a certain degree. It was known from this fact that the ground substance was also cementite underlying the carbon layer.

Table 2.

The electron diffraction pattern of the surface of the catalyser at the second stage of the reaction.

Values of Spacings observed by Electron Diffraction		Corresponding Indices of Graphite or Cementite.	
3.40 Å.	v.s.	(002) 3.39 Å.	
2.12	s.	(100) 2.12	
2.03	m.	(101) 2.02	
1.85	w.		(122), (113) 1.855 Å
1.69	m.	(004) 1.69	
1.228	s.	(110) 1.228	
1.17	m. diffuse.	(112) 1.150	
1.125	m. diffuse.	(006) 1.120	(240) 1.121
1.056	w.	(201) 1.049	(225) 1.050
0.981	w.	(106) 0.991	(413) (422) (340) 0.99

When the decomposition proceeded further, the surface of the cata-

lyser was covered all over by a carbon layer which took the powder form. The electron diffraction pattern was also attributed to carbon alone, and the cementite pattern could not be found already because of the existence of a thick layer of carbon.

On the Structure of Carbon produced by this Reaction. It has been pointed out that the crystal structure of so-called amorphous carbon is somewhat different from that of graphite⁽⁵⁾. In graphite, the three-dimensional atomic lattice is completed by a definite arrangement of atoms along every crystal axis. On the other hand, in amorphous carbon, the complete three-dimensional atomic lattice is not produced. It is made of pseudo-crystals, or it would be better to say, a kind of layer lattice consisting of hexagon planes of carbon atoms. The hexagon planes of carbon atoms are arranged in such a way that although they are parallel to each other along the *c*-axis, still along the *a*- or *b*-axis they are not arranged in any definite manner. For this reason, x-ray or electron diffraction patterns from amorphous carbons lack the spacings corresponding to the general indices (*hkl*) excepting (*hk0*) and (*00l*). As well known, the pattern of amorphous carbon consists of small numbers of diffused rings corresponding to (002), (100) and (110), and lacks other spacings such as (101) and (112) which are comparatively strong rings in the case of graphite. Thus, it may prove to be graphite, when the spacings corresponding to (101) and (112) be found in the pattern of carbon.

The observed pattern, as shown in Table 2, consists of many sharp rings. They can correspond to carbon and cementite respectively. There are also same spacings which can not be made distinct whether they are attributed to carbon or cementite, for the same values may be found in both substances. However, the spacings corresponding to the values of 2.03 Å can be attributed to graphite at least, for they are moderately strong in comparison with the ring of 1.85 Å, this latter being the typical ring of cementite. From this fact and the sharpness of reflected rings, the whole appearance of the pattern closely resembles the graphite pattern. It will be possible to conclude reasonably that the carbon formed at the early stage of the decomposition is not amorphous but is graphitized.

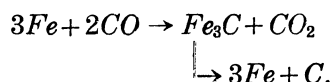
On the Poisoning Action by Oxygen. It has been known already that in this reaction the catalyser is poisoned by some substances such as sulphur or arsenic compounds⁽⁵⁾. We found that the reaction is also hindered by the existence of oxygen. When the pulverized iron was used as catalyser, the poisoning effect by the trace of oxygen was not so

(5) H. Akamatu, *J. Chem. Soc. Japan*, **64** (1943), 1251; H. Akamatu and K. Nagamatsu, *J. Colloid Science*, **2** (1947), 593.

remarkable as to be noticed. However, when an iron plate was used as catalyser, the decomposition did not proceed when a trace of oxygen existed in the carbon monoxide. In the latter case, we found that the oxide layer had been formed on the surface of the catalyser. By the electron diffraction, it was proved that the layer was made of Fe_3O_4 or sometimes of Fe_2O_3 .

Summary and Conclusion. It was found that carbon produced by catalytic decomposition of carbon monoxide by iron is not amorphous carbon as ordinary soot, but seems to be graphite, at least at the early stage of the decomposition. It was found by the electron diffraction that at the first stage of this reaction, cementite is formed on the surface of iron. It was also found that the catalytic decomposition of carbon monoxide never takes place if iron is oxidized before cementite is formed.

From these results, it will be concluded that carbon is produced by the decomposition of cementite, in other words, cementite is one of the intermediate compounds, at least, which is formed before free carbon is separated. This conclusion suggests that the reaction takes place following the schema as:



This conclusion is not far from that assumed by some of the former investigators. Some investigators have assumed that Fe_2C also is the other intermediate compound, but we have not yet found it by our experiments carried out at 500°C .

It is interesting also that carbon has the structure of graphite when it is separated from cementite.

In conclusion, the authors wish to express their thanks to Prof. J. Sameshima for his kind encouragement through the experiment. A part of the cost of this study was defrayed from the grant of the Ministry of Education, to which thanks are due.

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A Stereochemical Representation of the Structures and the Scission Reactions of Cholesterol Oxides.⁽¹⁾

By Yoshiyuki URUSHIBARA.

(Received February 7, 1949.)

In a previous paper⁽²⁾ the results of the studies on the scission reactions of the oxido ring in cholesterol oxides by the author and M. Chuman were briefly described. They include (i) reduction with sodium and amyl alcohol, (ii) catalytic reduction, (iii) action of aluminium amalgam and of aluminium isopropylate and isopropyl alcohol, (iv) hydration, and (v) action of Grignard's reagent. Besides those already cited there, the reactions of cholesterol oxides or their esters with hydrogen chloride,⁽³⁾ with acetic acid,⁽⁴⁾⁽⁵⁾ and with methanol in the presence of sulfuric acid,⁽⁴⁾ have been investigated by other authors. The results hitherto gathered may be summarized as follows:

The oxido ring in α -cholesterol oxide (I) or its esters is opened always but one exception between carbon atom 6 and the oxido oxygen atom, and the oxygen atom with the hydrogen atom derived directly or indirectly from the addenda forms a hydroxyl group attached to carbon atom 5 with the original α -configuration, while the residues from the addenda become attached to carbon atom 6, the configuration being determined to be β for certain residues, perhaps undetermined for the chlorine atom, assumed α for the methyl group from Grignard's reagent, and meaningless for the hydrogen atom from reduction (I $\rightarrow$ III). An exception is encountered in the reduction with sodium and amyl alcohol, where the oxido ring is opened between carbon atom 5 and the oxido oxygen atom, and the carbon atom 5 maintains the original α -configuration producing a cholestane derivative.

As for β -cholesterol oxide earlier works were carried out with impure specimens or the molecular compound with the α -isomeride, and the results obtained must be considered with reserve. Experiments with pure specimens have shown that the oxido ring in the β -oxide or its esters is opened, without exception, between carbon atom 5 and the oxido oxygen atom. The oxygen atom takes the hydrogen atom coming directly or

(1) An abridged account was read before the 68th annual meeting of the Chemical Society of Japan on October 18th, 1946.

(2) Y. Urushibara and M. Chuman, this Bulletin, 22 (1949), 69.

(3) F. S. Spring and G. Swain, *J. Chem. Soc.*, 1939, 1356; L. Ruzicka and W. Bosshard, *Helv. Chim. Acta*, 20 (1937), 244.

(4) J. Hattori, *J. Pharm. Soc. Japan*, 59 (1939), 411; 60 (1940), 334.

(5) M. Ehrenstein, *J. Org. Chem.*, 6 (1941), 626.

indirectly from the addenda and forms a hydroxyl group attached to carbon atom 6 with the original β -configuration, while carbon atom 5 cut off from the oxygen atom gains the residues from the addenda, and the configuration around this asymmetric centre is always α , as far as determined, giving rise to the formation of cholestane derivatives but never of coprostanane derivatives which might be expected (II $\rightarrow$ IV).

Ruzicka and co-workers⁽⁶⁾ constructed models for saturated and unsaturated sterols, where they related free or hindered rotation of the hydroxyl group at carbon atom 3 about the oxygen-carbon bond to the velocity of saponification of esters and took into account the flat molecular structures of the steroids demonstrated by Bernal. Thus, the free hydroxyl group of the cholestanol model and the hindered one in the coprostanol model were made to correspond respectively to the greater and the smaller velocities of the saponification of the esters. In the accompanying formulas, (V), (VI), and (VII), borrowed from their figures, substituents directed to the same side of (over, as generally formulated) the plane of the ring system are indicated by thick dots and letter S shows the cyclohexane ring concerned being in a chair form. If it is desired to visualize the actual models better than by these formulas, the pictures in the original paper may advisably be consulted.

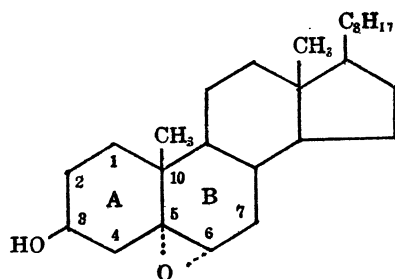
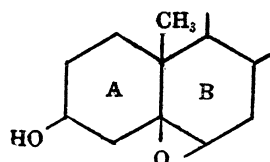
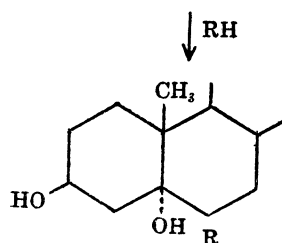
Although the formulas, and even the pictures of the models, hardly permit to perceive it at a glance, ring A has a chair form in the same manner of zigzag in cholestanol and in cholesterol, while in coprostanol the zigzag is in an inverse manner. In other words, if in the cholestanol and cholesterol models carbon atoms 1, 3, and 5 are situated downwards or at the bottoms of the zigzag, in the coprostanol model carbon atoms designated by the same numbers are placed upwards or at the tops of the zigzag. Moreover, in the cholestanol and cholesterol models an axis passes straight through the whole ring system, while the coprostanol model, owing to the cis linking of rings A and B, is remarkably folded at this linking.

An introduction of a double bond between carbon atoms 5 and 6 is possible only with ring A of cholestanol, and impossible with ring A of coprostanol, because the ethylene system will tend to be coplanar. On the other hand, a double bond can enter between carbon atoms 4 and 5 of ring A of either cholestanol or coprostanol; or, more precisely, the coplanar ethylene system comprising five carbon atoms 3, 4, 5, 6, and 10 and one hydrogen atom at 4 with a double bond between 4 and 5 is compatible with carbon atoms 1 and 2 as they are either in cholestanol or in coprostanol. The above consideration may be useful for reminding that Δ^5 -steroids are generally

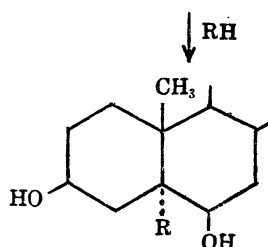
(6) L. Ruzicka, M. Furter, and M. W. Goldberg, *Helv. Chim. Acta*, 21 (1938), 498.

hydrogenated to cholestane derivatives⁽⁷⁾ and Δ^4 -steroids to either cholestane or coprostane compounds.

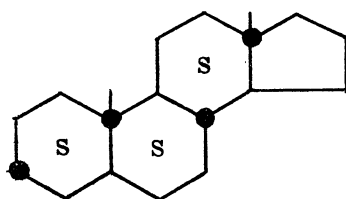
Now, the influence of a 5,6-oxido ring upon the form of ring A will be considered. The three-membered ring is equivalent or similar to

(I) α -Cholesterol oxide(II) β -Cholesterol oxide

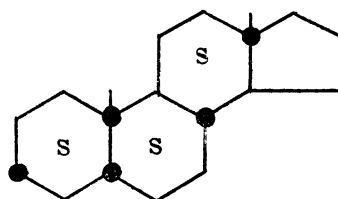
(III)



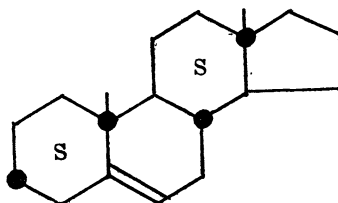
(IV)



(V) Cholestanol



(VI) Coprostanol



(VII) Cholesterol

(7) Cholestene gives two stereoisomeric hydrochlorides, J. Mauthner, *Monatsh.*, 28 (1907), 1113; T. Kon, *J. Pharm. Soc. Japan*, 65 (1945), 63, but is an explanation not plausible that pseudo-cholestene (coprostene) may intervene in the reaction?

the double bond in causing a structural restriction. The elements of symmetry found in the ethylene system still survive the destruction of the coplanarity by the three-membered ring introduced perpendicularly to the ethylene plane. Here, symmetry refers of course only to the arrangement or direction of the four atoms, other than the oxido oxygen atom, directly attached to carbon atoms 5 and 6, the nature of the four groups and the bond lengths being ignored. Thus, planes of symmetry in this sense exist within the segment of the molecule concerned, one passing through the three-membered ring and another through the oxygen atom and perpendicular to the former and to the bond between carbon atoms 5 and 6. The tendency of carbon atoms 10, 4, and 7 and the hydrogen atom at 6 to be arranged or directed symmetrically with reference to these planes excludes again ring A of coprostanol, irrespective as to whether the three-membered ring is α -oxidic or β -oxidic.

In this respect, not only α - but also β -cholesterol oxides must be considered as a derivative of cholestanol. When the β -oxide was called 5,6-epoxy-coprostanol-(3 β)⁽⁸⁾ by a term representing the structure, it was presumed automatically to be a coprostane derivative from the β -configuration of the linkage between carbon atom 5 and the oxygen atom; but in conformity with the real aspects of the spatial constitutions the β -oxide must be called 5,6 β -epoxy (or oxido)-cholestanol-(3 β), and 5,6 α -epoxy (or oxido)-cholestanol-(3 β) for the α -oxide cannot dispense with Greek letter α .

Before entering the next step of the stereochemical representation, the characteristics of the cleavage reactions of the oxido ring which are to be explained thereby will be summarized again in a shorter expression: The oxido ring in the α -oxide is ordinarily opened between carbon atom 6 and the oxygen atom, but can be split at the other linkage. Cleavage occurs always between carbon atom 5 and the oxygen atom in the β -oxide. The most important point is that cholestane derivatives, but none of coprostane derivatives, are produced in all the scission reactions of not only α - but also β -cholesterol oxide. Now, the stereochemical investigation affords a reasonable explanation of such behaviours of the oxides. Ring A in both α - and β -cholesterol oxides being of the same cholestanol type, the formation of cholestanol derivatives from both must be exclusive, as cholestanol is formed preferentially by the hydrogenation of cholesterol, unless a ring conversion takes place; and the formation of cholestanol derivatives from the α -oxide is possible for either of the alternative cleavage points, but that from the β -oxide is possible only when the oxido ring is opened between carbon atom 5 and the oxygen atom and thus when carbon atom 5 is given temporarily a free valency in order to be capable of adapting itself to ring A.

(8) Y. Urushibara, this Bulletin, 16 (1941), 182.

Suppose the oxido ring in the β -oxide were split between carbon atom 6 and the oxygen atom, then ring A of the cholestanol type and carbon atom 5 holding the oxygen atom in the β -configuration would be incompatible and must be reconciled only at the expense of an excessive work of either changing the former into the coprostanol type or inverting the latter to the α -configuration. While there may be no question as to stating that an inversion at carbon atom 5 would be difficult, or even impossible, so long as the oxygen atom remained attached there, the possibility of the conversion of ring A may be examined more closely. The conversion of ring A from the cholestanol type to the coprostanol type has been attained from Δ^5 -steroids through the versatile Δ^4 -ring, while the reverse ring conversion has been experienced, necessarily associated with the rearrangement of the configuration at carbon atom 5 from β to α , when a hydrogen atom is present at carbon atom 5 and at the same time a carbonyl group exists at an adjacent carbon atom, perhaps through an enolization and thus through a Δ^4 - or Δ^6 -intermediate. Such an inter-conversion of ring A involving a participation of an unsaturated intermediate could not be effected in a compound with an oxygen atom attached to carbon atom 5. A direct transformation of the cholestanol type into the coprostanol type might be possible, inasmuch as an oxygen atom bound to carbon atom 5 in the β -configuration were found favoring it, but it would not be so easy as expected from a mere consideration of the lability of a simpler cyclohexane ring, owing to the more profound difference between the cholestanol and the coprostanol rings and the structural restriction imposed by the surroundings. Thus, if the cleavage should occur between carbon atom 6 and the oxygen atom, then the process would be completed by giving a coprostanol derivative resulting from the conversion of ring A rather than a cholestanol derivative requiring the inversion at carbon atom 5; but even the trouble involved in this ring conversion appears to be enough for preventing such a fission from taking place and for giving way to the other fission that can be settled more smoothly. In other words, the linkage will resist such a fission as would be associated with more later work. It may be again emphasized in this connection that a transformation of ring A does not take place even in the hydrogenation of Δ^5 -steroids. The hydroxyl group or its equivalent at carbon atom 3 may add the difficulty in the ring conversion, because the group freely rotatable in the cholestanol type must be confined in a sterically hindered position when the ring is converted into the coprostanol type, and it may be logically correct to mention that such a confinement itself will be confronted with a steric hindrance.

In the preceding paragraphs the structures of cholesterol oxides and the courses of scission reactions of the oxido ring in them have been elucidated on the basis of the spatial formulation elaborated by Ruzicka

and co-workers. If the stereochemical representation be feasible also in the cases of the oxides of other Δ^5 -steroids, then the behaviours in scission reactions will give grounds for discussing the configuration of their oxido rings. Thus, in a separate paper it will be shown that the oxido rings in the oxides of Δ^5 -cholestenone possess most probably the configurations contrary to the Greek letters arbitrarily prefixed in their names.

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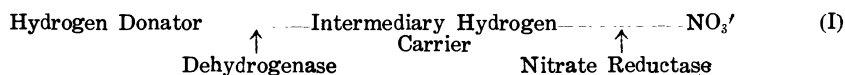
Studies on Nitrate Reductase. III.⁽¹⁾⁽²⁾

By Ryo SATO and Fujio EGAMI.

(Received February 1, 1949.)

Introduction. Many species of bacteria are able to reduce nitrate to nitrite. The actual agency of this reduction, however, remained obscure until Quastel, Stephenson and Whetham⁽³⁾ pointed out the existence of a specific enzyme acting on nitrate in *Bac. coli* and some other facultative anaerobes. In 1938-39 Yamagata⁽⁴⁾ obtained a cell-free preparation of this enzyme and proposed the name "nitrate reductase" instead of "nitrata~~se~~" which had been previously used. Recently we have succeeded in obtaining a cell-free preparation of nitrate reductase from *Bac. coli* by ultrasonic destruction of the cells and studied several properties and the mode of action of this enzyme.⁽¹⁾⁽²⁾

By these foregoing investigations it has been firmly established that nitrate reductase is an enzyme which catalyzes the oxidation of the reduced form of an intermediary hydrogen carrier by nitrate and therefore the biological reduction of nitrate consists of two steps even in the simplest case. This case may be shown schematically as follows:



As the intermediary hydrogen carrier in this scheme, methylene blue or

(1) F. Egami and R. Sato, *J. Chem. Soc. Japan*, **68** (1947), 39.

(2) F. Egami and R. Sato, *J. Chem. Soc. Japan*, **69** (1948), 20; cf. F. Egami, *Chemical Researches*, **1** (1948), 117.

(3) J. H. Quastel, M. Stephenson and M. D. Whetham, *Biochem. J.*, **19** (1925), 304; cf. L. H. Stickland, *Biochem. J.*, **29** (1934), 1543; E. Aubel, *Enzymologia*, **4** (1937), 51, etc.

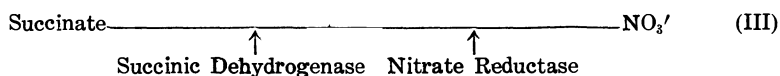
(4) S. Yamagata, *Acta Phytochimica*, **10** (1938), 283; **11** (1939), 145.

any other suitable oxidation-reduction indicator can be used *in vitro*. For the purpose of the study of nitrate reductase apart from dehydrogenase system, we have constructed the following system.



Here the leuco form of methylene blue is prepared chemically by catalytic hydrogenation of methylene blue using Pd-BaSO₄ as a catalyst.

Further we have shown that flavin-adenine-dinucleotide, and presumably also several flavoprotein enzymes, can act as intermediary hydrogen carriers. However we found an important exception to scheme (I) when succinate was supplied as a hydrogen donator. In this case the succinate-succinic dehydrogenase system can react directly with the nitrate-nitrate reductase system without any intermediary hydrogen carrier.



It must be mentioned here that succinic dehydrogenase is known as a so-called "cytochrome reducing dehydrogenase".

All these findings provide an interesting information about the position of nitrate reductase in the reaction chains of biological oxidations. That is, nitrate reductase may perhaps play a similar rôle to that of the Warburg-Keilin system when nitrate is used as an ultimate hydrogen acceptor instead of molecular oxygen.

From these considerations we have been led to an assumption that the chemical nature of nitrate reductase might be similar to that of cytochrome or cytochrome oxidase. In the present paper studies on this line will be reported.

Experimental. Preparation of enzyme: *Bac. coli* was grown on peptone-bouillon-agar medium containing 0.1 % KNO₃ for 24 hours at 37°. Cells were harvested and washed several times with 0.8 % NaCl solution and suspended thickly in phosphate buffer (pH 7.4, $\frac{1}{10}$ mol). The suspension was then exposed to ultrasonic waves (500 KC., anode voltage 1200 volts) for 30 minutes and was centrifuged (10,000 r.p.m.) to remove cell debris completely. The supernatant fluid was dialysed overnight against streaming water. To this solution ammonium sulfate was added to an extent of 0.2 saturation and the precipitate was centrifuged off. Ammonium sulfase was again added to half saturation, and then centrifuged. The precipitate thus obtained was dried in a vacuum desiccator containing concentrated sulfuric acid. Thus we could obtain from ca. 50 g. wet cells ca. 1 g. of dried powder mixed with crystals of ammonium sulfate.

This preparation can be kept for several months without inactivation in a desiccator at 0°. 300 mg. of this powder was dissolved in 10 c.c. of distilled water and used as a nitrate reductase solution. Besides nitrate reductase our preparation shows a powerful activity of formic dehydrogenase when tested with methylene blue technique. For the purpose of spectroscopic observations solutions containing 100 mg. of powder per c.c. were used.

Measurement of enzyme activity: Thunberg tubes were employed. Reaction mixture was usually as follows: 0.5 c.c. of enzyme solution, 1 c.c. of phosphate buffer (pH 7.4, $\frac{1}{10}$ mol), 1 c.c. of KNO_3 solution ($\frac{1}{100}$ mol), 2 c.c. of leucomethylene blue ($\frac{1}{50}$ mol), and 1 c.c. of inhibitor solution or distilled water. The tube was incubated for 1 hour at 37° and the nitrite thus formed was determined.

Determination of nitrite: The reaction mixture was decolorized by activated charcoal and proteins were removed. Then Griess-Ilosvay's reagent was added and the pink color thus developed was determined colorimetrically with Pulfrich's stufenphotometer.

Effects of Inhibitors. In order to elucidate the chemical nature of nitrate reductase, we have studied the effects of some typical respiratory inhibitors on the action of this enzyme. The results of this experiment are summarized in Table 1.

Table 1.

Inhibitors.....	KCN			NaN ₃		CO		monoiodo- acetic acid	cysteine	cystine	
Concentrations.... (mol/l.)	10 ⁻⁴	10 ⁻³	10 ⁻²	10 ⁻³	10 ⁻²	1 atm. (dark)	1 atm.* (light)	10 ⁻³	10 ⁻²	2×10 ⁻²	2×10 ⁻²
Degrees of in- hibition (%)	7	97	100	56	100	42	0	52	93	92	7

* The tube was illuminated by 100 watt lamp from a distance of 30 cm.

As is shown in Table 1, nitrate reductase is markedly inhibited by so-called "heavy metal reagents" such as KCN, NaN₃ and CO. This fact strongly suggests that a certain heavy metal is related to the activity of this enzyme. In fact Quastel⁽⁵⁾ already assumed the participation of iron in the bacterial reduction of nitrate on the basis of his observation with resting bacteria. Our experiment with cell-free enzyme also indicates in accordance with his assumption that the heavy metal contained in nitrate reductase must be iron, because we have shown, as is recorded in Table 1, that CO-inhibition of nitrate reductase completely disappears by light and it is well known that among CO-compounds of various heavy metals and their complexes, so far as examined, only those of iron and its complexes are photodissociable and therefore their catalytic activities, if any,

(5) J. H. Quastel, *Nature*, 130 (1932), 207; cf. H. Burström, *Planta*, 29 (1939), 292.

will be restored by light.

Although the above experiment is not sufficient to acquire an accurate knowledge about the rôle of iron in the process of enzymic reduction, it seems very attractive for us to consider that the essential function of the iron consists in an alternative cycle of valency between ferric and ferrous states, since nitrate reductase is inhibited both by KCN and CO; the former combines with ferric iron in almost all cases and the latter solely with ferrous iron.

In addition it must be noticed that this enzyme is intensively inhibited by a low concentration of monoiodoacetic acid, a specific inhibitor for sulfhydryl enzyme. Cysteine is also poisonous, but cystine is almost without effect. These facts seem to show that the sulfhydryl ($-SH$) or disulfide ($-S-S-$) group may be connected with the activity in some manner.

Spectroscopic Observations. The crude preparation of nitrate reductase obtained by our method shows a brownish yellow color in a concentrated aqueous solution. This solution, when reduced by $Na_2S_2O_4$, exhibits three absorption bands in the visible region under Zeiss microspectrometer. The non-reduced solution shows only very weak and diffused absorptions (oxidized bands). The positions of the three reduced bands are as follows:

- (1) $585 m\mu$, very weak and diffused.
- (2) $560 m\mu$, intense and sharp.
- (3) $530 m\mu$, weak and sharp.

Among these bands, (2) and (3) are apparently identical with the α - and β -bands of cytochrome b which were observed by Keilin⁽⁶⁾ with *Bac. coli* suspension. In contrast with (2) band (3), band (1) is very weak and diffused, the origin of which is yet unknown.

In order to decide whether there exists any relationship between nitrate reductase and these bands, the following experiments have been carried out. The enzyme solution was precipitated fractionally into five portions by acetone (below 0°) and the activity of nitrate reductase and intensities of the reduced bands were determined. The results are shown in Table 2.

Table 2.

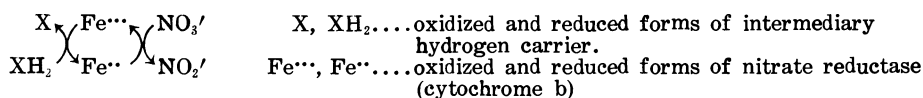
Fractions	Volume % of acetone when precipitated	Relative activities of nitrate reductase	Intensities of	
			the band at $585 m\mu$	the bands at 560 and $530 m\mu$
I	0 —33.3	100	+	+++
II	33.3—50	15	+	+
III	50 —66.6	4	++	±
IV	66.6—75	0	—	—
V	75 —88.3	0	—	—

Further addition of acetone produced no precipitate.

(6) D. Keilin, *Ergeb. Enzymforsch.*, 2 (1933), 239.

The following facts have been made clear by these results: (1) the band at $585\text{ m}\mu$ has no relation to nitrate reductase, and (2) the intensities of the bands at $560\text{ m}\mu$ and $530\text{ m}\mu$, which are regarded as the reduced bands of cytochrome b, are apparently parallel with the activity of this enzyme. This parallelism seems to be an evidence, though not decisive, of the identity of cytochrome b with nitrate reductase. That nitrate reductase may contain iron as an essential component (as postulated by our inhibition studies) also agrees with this assumption, for cytochrome b is an iron-porphyrin enzyme.

We have further attempted some experiments to ascertain the identity of these two substances. If our assumption is correct and nitrate reductase (= cytochrome b) undergoes cyclic oxidation and reduction, the process of enzymic reduction of nitrate may be shown by the following scheme.



From this scheme it is expected that the reduced bands of cytochrome b will shift to the oxidized bands when nitrate is added. We found, contrary to our expectation, that no change occurs in the absorption bands of cytochrome b, previously reduced by $\text{Na}_2\text{S}_2\text{O}_4$, even when a large amount of nitrate was added. This fact is not, however, contradictory with our assumption, since we later found that the enzyme treated with $\text{Na}_2\text{S}_2\text{O}_4$ loses its activity irreversibly. To avoid the use of $\text{Na}_2\text{S}_2\text{O}_4$ we then adopted the following method. In the main room of a Thunberg tube 3 c.c. of enzyme solution, 0.5 c.c. of sodium formate (1 mol), and 0.5 c.c. of methylene blue (1:10,000) were put in. In the side chamber of the tube was placed 0.5 c.c. of KNO_3 (2 mol). Then the tube was evacuated and incubated at 37° . As our enzyme preparation contains powerful formic dehydrogenase as well as nitrate reductase the methylene blue was soon decolorized and simultaneously the reduced bands of cytochrome b appeared. After complete decolorization of methylene blue KNO_3 was mixed with the enzyme solution. Then immediately decrease of the intensities of the bands of reduced cytochrome b was observed and they approached those of oxidized form. But this conversion ceased incompletely probably due to an establishment of an equilibrium between the oxidizing power of nitrate and the reducing tendency of formic dehydrogenase system. This result seems to support our assumption firmly.

It is quite natural to expect then that some changes will take place by KCN and NaN_3 in the absorption bands of cytochrome b, since these reagents inhibit nitrate reductase markedly. But we could not observe any change of absorption spectrum by KCN and NaN_3 in either the

oxidized or reduced enzyme solution. Reduced cytochrome b has not only α - and β -bands, but also γ -band at about $430\text{ m}\mu$ which can not be observed by this method. As the possibility still remains that γ -band will be affected by these inhibitors, we will study this point in future.

Discussion. Although many problems are still left unsolved about the chemical nature of nitrate reductase, the identity of this enzyme with cytochrome b becomes quite probable by our present investigations.

Cytochrome b is widely distributed in aerobic cells and is considered as an important factor of aerobic cell respiration, but studies on this substance have been neglected compared with other components of the cytochrome system. Up to the present it has been investigated mainly by spectroscopic method and it is now confirmed that there are two kinds of cytochrome b whose absorption bands lie at somewhat different positions. As one of them is present in the heart muscle of animals etc. and the other in *Bac. coli*, etc., we will distinguish them as the heart muscle type and *Bac. coli* types respectively. The positions of the reduced bands are as follows :

	α -band	β -band
Heart muscle type	$564\text{ m}\mu$	$534\text{ m}\mu$
<i>Bac. coli</i> type	$460\text{ m}\mu$	$630\text{ m}\mu$

To which component of cytochrome b must be attributed the activity of nitrate reductase? We assume that cytochrome b of *Bac. coli* type is the very nature of nitrate reductase and that of the heart muscle type is unconcerned with this enzyme. This assumption also answers the question why there are tissues and cells which can not reduce nitrate in spite of a high content of cytochrome b.

We have further clarified by consulting "Bergey's Manual of Determinative Bacteriology"⁽⁷⁾ and Tamiya and Yamaguchi's⁽⁸⁾ list on cytochrome types of microorganisms that (1) bacteria without cytochromes can not reduce nitrate at all, (2) almost all organisms containing cytochrome b of *Bac. coli* type can reduce nitrate, but those of the heart muscle type are not able to reduce nitrate except in a few cases. Moreover Bernheim and Dixon⁽⁹⁾ reported that among various tissues of many animals only the liver (and also the muscle of a few species) can reduce nitrate, while according to Yoshikawa⁽¹⁰⁾, cytochrome b of the liver is *Bac. coli* type. This parallelism between the ability of nitrate reduction and the existence

(7) D. H. Bergey, "Bergey's Manual of Determinative Bacteriology", 4th Ed., Baltimore (1934).

(8) H. Tamiya and S. Yamaguchi, *Acta Phytochimica*, 6 (1934), 105.

(9) F. Bernheim and M. Dixon, *Biochem. J.* 22 (1928), 125.

(10) H. Yoshikawa, from discussions at the 1st "Symposium on Enzyme Chemistry" held at Tokyo in October, 1948.

of *Bac. coli* type cytochrome b also seems to be favourable for our assumption.

Summary.

The effects of various inhibitors on nitrate reductase have been investigated and some spectroscopic observations have been made to elucidate the chemical nature of nitrate reductase. From these studies it becomes very probable that cytochrome b of *Bac. coli* type is identical with nitrate reductase.

The authors express their sincere thanks to Prof. H. Tamiya for his kind suggestion to the present studies, and also to Prof. S. Hosoya for his kindness in granting many conveniences for these experiments.

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If the heat treatment is omitted after the deposition of the cadmium film, we can observe no new peak of spectral sensibility.

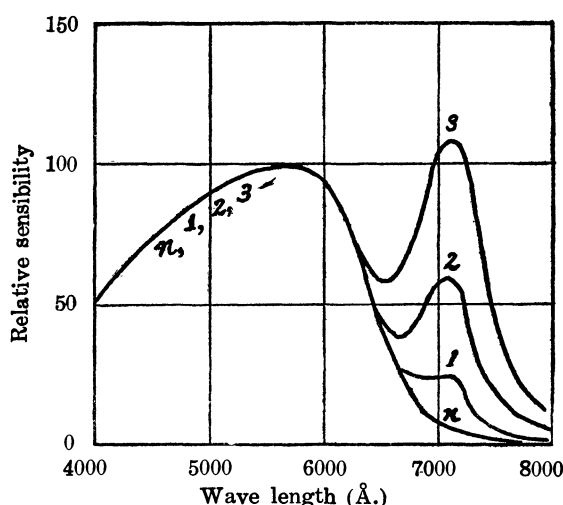


Fig. 1. Spectral sensibility of the cells.

The curve *n* is one of a normal cell.

detection utilizing the reflection method of electron diffraction was used for a sample which was made by the heat treatment of 4 hours at 200°C in vacuum. As usual the cadmium film of the order of 10 μ thick was deposited on the selenium semiconductor by evaporating in vacuum before the heat treatment. The result of the electron diffraction shows the existence of a CdSe layer of the zinc blend type.

Next, the author measured the spectral transmission of CdSe which was deposited on a glass plate by the vacuum evaporation. This CdSe was made by the wet method, namely, by using the reaction of $\text{Cd}^{++} + \text{H}_2\text{Se} \rightarrow \text{CdSe} + 2\text{H}^+$. The transmission curve is in Fig. 3.

Discussion of the Experiments.

It is clear that the new peak of 7100 Å is caused by the heat treatment. The author has already explained the process of the reaction of cadmium and selenium semiconductor by

To have knowledge of the change of the rectification by the heat treatment, another sample is made which has a thick cadmium film evaporated in vacuum on the selenium semiconductor. Its static characteristics of rectification are measured before and after the heat treatment of 1 hour at 100°C. The result is shown in Fig. 2. The resistance of the barrier layer becomes very large by the heat treatment.

On the other hand, to see what substance is created on the selenium by the heat treatment, a direct method of

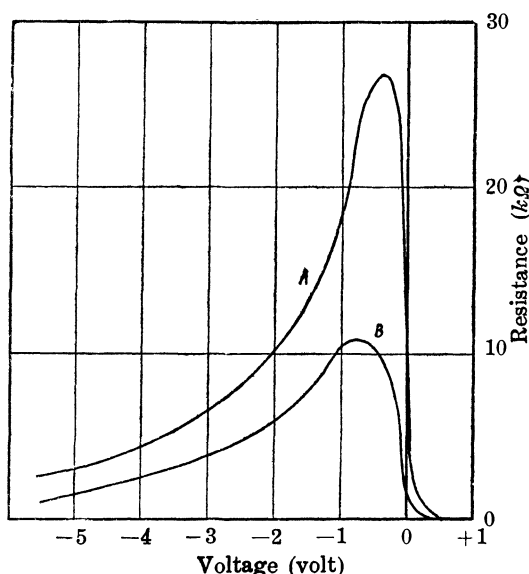


Fig. 2. Characteristics of rectification before (B) and after (A) the heat treatment.

finding a thermoionic current occurring at a contact of both materials.⁽²⁾ By the increase of the mobility owing to high temperatures, cadmium ions

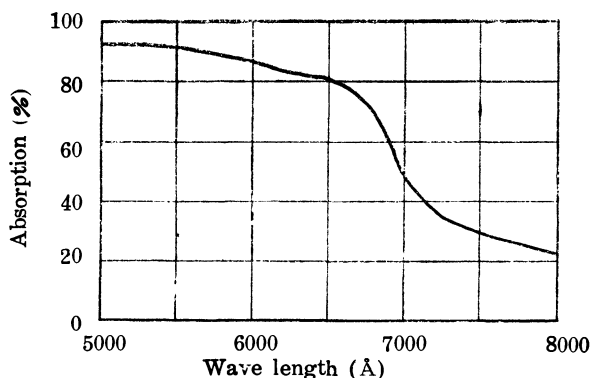


Fig. 3. Absorption spectrum of CdSe film.

accelerated by the internal field move through the CdSe layer at the contact and the layer of CdSe grows with the flowing of ionic current in the external circuit. This means just the converting process of the free energy difference in the reaction $\text{Cd} + \text{Se} \rightarrow \text{CdSe}$ into the electric energy.

The fact that the CdSe layer is found on the selenium by the electron diffraction tells us that the entire layer of the cadmium deposited on the selenium has reacted with the selenium.

In this way the barrier layer of the new photoelement is composed of double layers; the CdSe layer and selenium layer over which the internal

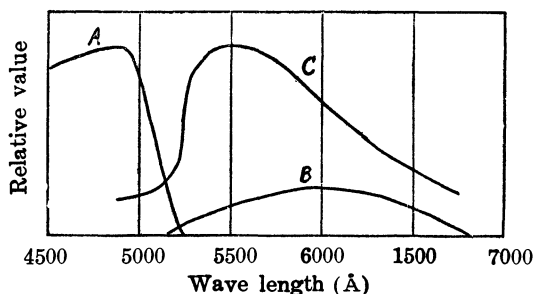


Fig. 4 (b). Spectral absorption (A, B) and photoconductivity (C) of CdS⁽⁴⁾.

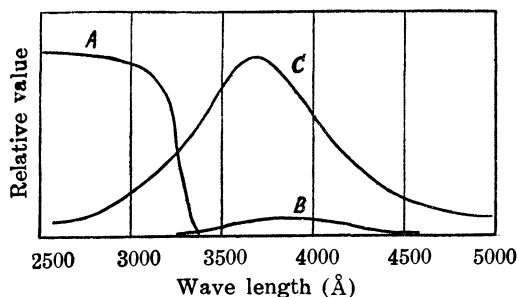


Fig. 4 (a). Spectral absorption (A, B) and photoconductivity (C) of ZnS⁽⁴⁾.

field extends. If the light is put on the layer, it is first absorbed in the CdSe layer and next in the selenium layer. Then the normal peak of the spectral sensibility is attributed to the internal photoeffect of the selenium and the new peak of 7100 Å to the one of the CdSe layer.

It has been reported that CdSe has the internal

(2) M. Tomura, this Bulletin, 22 (1949), 82.

photoeffect.⁽³⁾ From the spectral sensibility of the internal photoeffect and spectral absorption of ZnS and CdS, the following hypothesis to explain the barrier layer photoeffect of CdSe is given.

Fig. 4 shows the spectral absorption and internal photoeffect of ZnS and CdS.⁽⁴⁾ The absorption in the visible range corresponds to the transition of electrons from the filled band to the excited states. The tails of the absorption curve, that is $3800\text{\AA}$ of ZnS and $6000\text{\AA}$ of CdS, correspond to the transition of electrons from the impurity levels to their excited states. The fact that the peak of the sensibility of the internal photoeffect coincides with the peak of the absorption by the impurities means that photoelectrons excited by the absorption of light enter into the conduction band from the excited states by absorbing thermal energy and contribute to the conduction.⁽⁵⁾

From the shape of the long wave end of the spectral absorption curve of CdSe measured by the author, we presume that the characteristic absorption of CdSe extends to the region of the absorption curve by the impurity centre. Consequently the internal photoeffect is expected at the long wave end as well as ZnS and CdS.

As the heat treatment is long enough in duration and high enough in temperature to convert the cadmium film to the CdSe layer; the thicker the cadmium film, the thicker is the CdSe layer formed.

Consequently the light quantity absorbed in the CdSe layer becomes greater relative to the one in the selenium layer when the cadmium film becomes thicker, making the height of the new peak higher with the thickness of the cadmium layer.

As for the rectification, a remarkable change of the resistance after the heat treatment supports the formation of the CdSe layer. By the formation of the CdSe layer, the potential hill to the stream of the positive hole becomes higher at the contact, resulting in the increase of the resistance of the barrier layer.

Conclusions. A selenium barrier layer photoelement which has a new process of heat treatment in its making is formed, having a new peak in its spectral sensibility curve. This peak is attributed to the internal photoeffect of the CdSe layer which is made in the barrier layer by the heat treatment.

From the above discussions, it is concluded that if there are photoconductive substances in the barrier layer of the selenium barrier layer cell where the internal field influences, these substances show their own barrier layer photoeffect when they absorb the light corresponding to the internal photoeffect.

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(3) R. Freirehs, *Phys. Rev.*, **72** (1947), 594.

(4) J. H. Gisolf, *Physica*, **6** (1939), 81; F. A. Kröger, *ibid.*, **7** (1940), 1; B. Gudden and R. W. Pohl, *Z. Physik*, **2** (1920), 181.

(5) F. Seitz, *J. Chem. Phys.*, **6** (1938), 454.

On the Equilibrium of the Radioactive Elements in the Hydrosphere. V.⁽¹⁾ A Simple Method for Distinguishing Uranium and Thorium in Radioactive Minerals.

By Kazuo KURODA

(Received November 16, 1948.)

It was found that the uranium and thorium in radioactive minerals are easily distinguished by measuring the radioactivity of radium emanation and thorium emanation in the minerals. Though this method is a qualitative one, it may be improved in future and it will be used as a quantitative method for determining the ratio of uranium to thorium in radioactive minerals.

Method of Experiment. Several grams of powdered minerals are taken in a vessel, and 50 to 100 c.c. of water are added. The radioactivity of the water is measured on the next day. The water is taken with an injector (about 50 c.c.), as quickly as possible, and the radioactivity is measured at once. In the case of thorium minerals, a rapid decay curve of thorium emanation will be obtained and in the case of uranium minerals, on the other hand, the radioactivity will increase gradually as the result of the formation of the decay products of the radium emanation. In the case of radioactive minerals containing both series of radioactive elements, the radioactivity of radium emanation and thorium emanation will be simultaneously observed.

Results of Experiment. (a) Pitchblende. The powdered sample of pitchblende (about 3 grams) was immersed in distilled water (about 50 c.c.) overnight. A 20 c.c. portion of the water was taken with an injector, as quickly as possible, and it was ejected in the ionization chamber of I.M. fontactoscope. The radioactivity measurement was commenced at once. An example of the experiments is shown in Table 1.

The concentration of radium emanation in the water was calculated to be about 300 Mache. The radioactivity of thorium emanation

Table 1. Pitchblende.

Time (min.)	Radioactivity (div./min.)
1	7.7
2	7.3
3	9.0
4	9.5
5	10.5
6	13.5
7	13.0
16	16.7
17	17.0

(1) Previous Paper. IV. K. Kuroda and Y. Yokoyama, this Bulletin, 22 (1949), 43.

was not observed, as the thorium content of pitchblende was low usually.

(b) Monazite. The powdered sample of monazite (10 grams) was immersed in the distilled water overnight. A 45 c.c. portion of the water was taken with an injector, as quickly as possible, and it was ejected in the ionization chamber of I.M. fontactoscope. The radioactivity measurement was commenced at once, and the following result was obtained (Table 2).

Table 2. Monazite.

Time (min.)	Radioactivity (div./min.)
1	2.4
2	1.2
3	0.8
4	0.8
5	0.5
6	0.7
7	0.4
8	0.6
9	0.7
10	0.4

Table 2 shows that the thorium emanation dissolves out from the mineral, but the radium emanation does not.*) The concentration of thorium emanation in the water is calculated to be about 30 Tn-Mache.

(c) Enalite. The thorium content of this mineral is about 55 per cent and the uranium content is about 25 per cent. Therefore, it may be expected that both thorium

emanation and radium emanation will dissolve out from this mineral, when it is treated as described above.

The powdered sample of enalite (about 40 grams) was immersed in the distilled water (100 c.c.) overnight. A 70 c.c. portion of the water was taken with an injector, and it was ejected in the ionization chamber of I.M. fontactoscope. The result of the experiment is shown in Table 3.

Table 3. Enalite.

Time (min.)	Radioactivity (div./min.)
1	3.6
2	2.0
3	1.4
4	1.7
5	1.7
10	1.6
11	1.6
12	1.9
13	1.7
34	2.0
35	2.1
36	2.1
37	2.4

The concentration of thorium emanation in the water is about 40 Tn-Mache and that of radium emanation is about 10 Mache.

Summary.

It was found that the uranium and thorium in radioactive mineral are easily distinguished by measuring the radioactivity of radium emanation and thorium emanation in the minerals with I.M. fontactoscope.

The author expresses his hearty thanks to Professor Kenjiro Kimura for his kind guidance. The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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*) Natural leak is about 0.5 div./min.

On the Diamagnetism of Perylene. II*.

By Genjiro HAZATO

(Received November, 17, 1948.)

In a preceding paper,⁽¹⁾ we have shown a simple method to compute the diamagnetic anisotropy of aromatic molecules from the experimental values of powdered crystals, and we have found that perylene molecule has an anisotropic part about twice as large as that of naphthalene.

In general, aromatic molecules show abnormally large diamagnetic anisotropy, the susceptibility being maximum if the direction of the impressed field is perpendicular to the molecular plane, and minimum if the two are parallel with each other. To explain this phenomenon, it was assumed by several authors⁽²⁾ that in these molecules the diamagnetic currents might circulate from one atom to the other along the aromatic ring system. In other words, at each carbon atom, constituting the aromatic ring system, there is a π - or p_z -electron which is free to move, under the influence of the magnetic field, from one carbon atom to the adjacent one. This is closely analogous to the electric current induced in a conducting network. This hypothesis has come to be generally accepted in qualitative explanations.

Starting from the above consideration, quantitative interpretations of the anisotropic parts of the aromatic molecules have been worked out by Pauling⁽³⁾ and by London⁽⁴⁾. Pauling's argument is based essentially on classical ideas, assuming that the aromatic rings should behave like superconductors.⁽⁵⁾ London uses a quantum mechanical procedure, based on Hückel's molecular orbital treatment, extending to the case of the presence of a magnetic field. He calculated the ratios of the anisotropies of various condensed aromatic compounds to that of benzene, obtaining excellent agreement with experiment.

Here, in this paper, we shall apply the London theory to the theoretical calculation of the anisotropic part of perylene molecule, seeing how far the theory can carry us. The present calculation follows, for convenience' sake, the same notation and procedure as London's paper.⁽⁴⁾

London's secular equation is as follows:

$$|\eta_{kl} \exp 2\pi i f_{kl} - x \delta_{kl}| = 0 \quad (1)$$

$$\text{Here } \eta_{kl} \begin{cases} 1 & \text{if } k \text{ is a neighbor of } l \\ 0 & \text{if } k \text{ is not a neighbor of } l \end{cases} \quad \delta_{kl} \begin{cases} 1 & \text{if } k = l \\ 0 & \text{if } k \neq l, \end{cases}$$

*) This paper was read at the annual meeting of the chemical constitution of the Chem. Soc. of Japan in Oct. 1946 and in Apr. 1948.

(1) H. Shiba, and G. Hazato, this Bulletin, **22** (1949), 92.

(2) P. Ehrenfest, *Physica*, **5** (1925), 388; *Z. Phys.*, **58** (1929), 719; C. V. Raman, and K. S. Krishnan, *Proc. Roy. Soc. (London)*, **A**, **113** (1927), 511; C. V. Raman, *Nature*, **123** (1929), 945; K. Lonsdale, *Proc. Roy. Soc. (London)*, **A**, **159** (1937), 149.

(3) L. Pauling, *J. Chem. Phys.*, **4** (1936), 673.

(4) E. London, *J. du Physique*, **8** (1937), 397.

(5) Cf. F. London, *J. Chem. Phys.*, **5** (1937), 837.

and

$$x = \frac{E^{(1)} - W_0}{W_1} \quad (2)$$

$E^{(1)}$ is the ordinary first order perturbation energy:

$$E^{(1)} = E - E^{(0)}, \quad (3)$$

$E^{(0)}$ is the energy of the zeroth order approximation under the influence of the magnetic field, which is expressed by

$$E^{(0)} = E^{(00)} + \frac{1}{2} \chi H^2, \quad (4)$$

where χ is the susceptibility contribution of the π -electron (one per aromatic carbon atom), and H is the field strength. In equation (2), W_0 is the Coulomb integral independent of the magnetic field, W_1 is the ordinary exchange integral of the nearest neighbors of the orbital theory in the absence of the magnetic field, and in this case, this is used as a unit of the energy scale. In equation (1),

$$\exp(2\pi i f_{kl}) = W_{kl}/W_1 \quad (5)$$

and

$$f_{kl} = (e/hc) H \cdot S_{kl}, \quad (6)$$

in which W_{kl} represents the exchange integral in the presence of the magnetic field, S_{kl} is the area of the triangle formed by the neighbors k , l and the origin, arbitrarily chosen in the plane of the molecule, therefore, f_{kl} can be considered as a numerical value proportional to the magnetic flux.

Following the above conditions and the model shown in Fig. 1, the secular determinant of perylene molecule can be arranged in the form

$$\begin{vmatrix} 0 & 1 & 2 & 3 & 4 & 0' & 4' & 3' & 2' & 1' & \bar{1}' & \bar{2}' & \bar{3}' & \bar{4}' & \bar{0}' & \bar{4} & \bar{3} & \bar{2} & \bar{1} & \bar{0} \\ 0 & -x \epsilon_1^* & & & & 1 & & & & \epsilon_1 & & & & & & & & & & \\ 1 & \epsilon_1 & -x & 1 & & & & & & & & & & & & & & & & a \epsilon_1^* \\ 2 & & 1 & -x & \epsilon_2 & & & & & & & & & & & & & & & \\ 3 & & & \epsilon_2^* & -x & \epsilon_3 & & & & & & & & & & & & & & \\ 4 & & & & \epsilon_3^* & -x & \epsilon_2 & & & & & & & & & & & & & \\ 0' & 1 & & & & \epsilon_2^* & -x & \epsilon_2 & & & & & & & & & & & & \\ 4' & & & & & & \epsilon_2^* & -x & \epsilon_3 & & & & & & & & & & & \\ 3' & & & & & & & \epsilon_3^* & -x & \epsilon_2 & & & & & & & & & & \\ 2' & & & & & & & & \epsilon_2^* & -x & 1 & & & & & & & & & \\ 1' & & & & & & & & & 1 & -x & a \epsilon_1 & & & & & & & & \\ \bar{1}' & \epsilon_1^* & & & & & & & & & a \epsilon_1^* & -x & 1 & & & & & & & \epsilon_1 \\ \bar{2}' & & & & & & & & & & & 1 & -x & \epsilon_2 & & & & & & \\ \bar{3}' & & & & & & & & & & & & \epsilon_2^* & -x & \epsilon_3 & & & & & \\ \bar{4}' & & & & & & & & & & & & & \epsilon_3^* & -x & \epsilon_2 & & & & \\ \bar{0}' & & & & & & & & & & & & & & \epsilon_2^* & -x & \epsilon_2 & & & 1 \\ \bar{4} & & & & & & & & & & & & & & & \epsilon_2 & -x & \epsilon_3 & & \\ \bar{3} & & & & & & & & & & & & & & & & \epsilon_3^* & -x & \epsilon_2 & \\ \bar{2} & & & & & & & & & & & & & & & & & \epsilon_2^* & -x & 1 \\ \bar{1} & & & & & & & & & & & & & & & & & & 1 & -x & \epsilon_1^* \\ \bar{0} & & & & & & & & & & & & & & & & & & & \epsilon_1 & -x \end{vmatrix} = 0, \quad (7)$$

Substituting (4) in (3), and by means of the partial differentiation with regard to H , a susceptibility contribution of a π -electron becomes

$$\chi_p = - \left(\frac{\partial^2 E^{(1)}}{\partial H^2} \right)_{H \rightarrow 0} \quad (11)$$

Since equation (8) has the form: $F_1(x) + (2\pi f)^2 \cdot F_2(x) = 0$, let x' be a root of $F_1(x) = 0$, and the corresponding root of (8) will be expressed approximately by

$$x = x' + x'' (2\pi f)^2, \quad (12)$$

in which

$$x'' = \frac{F_2(x')}{F_1'(x')},$$

F_1' represents the first derivative of F_1 with regard to x .

From (9), (10), (11) and (12), we obtain London's final result:

$$\Delta\chi = 2 \sum_{p=-\frac{N-2}{4}}^{\frac{N-2}{4}} \chi_p = -4 \sum (x'') |W_1| \left(\frac{2\pi e S_B}{\hbar c} \right)^2. \quad (13)$$

Here, the half of the lowest levels is completely occupied by all the electrons in question, so that each level may be occupied by a pair of electrons, each pair having antiparallel spin directions.

In equation (13), we can take both W_1 and S_B as constants throughout the model constructed by the same regular hexagons. But, in the present case, as is the case with Fig. 1 or equation (8), the area S_B of the central hexagon would be somewhat affected by α , that is, the distance $1\bar{1}$ or $1'\bar{1}'$ would be a function of α ; the smaller the value of α becomes, the larger the S_B becomes. In spite of this fact, as it will be shown in a later paper, there is enough reason why we can ignore the S_B -effect of the central hexagon. Consequently, assuming W_1 and S_B to be constants, $\Delta\chi$ must directly be proportional to $\Sigma(x'')$; moreover, even if we take the parameter α as a variable, the corresponding values of $\Sigma(x'')$ may depend almost entirely upon the values of α only.

Now, all we have to do is to compute each numerical value of $\Sigma(x'')$ for each value of α . The solutions of equation (8) are shown in Table 1.

The notation x''' in the table represents the corresponding value of x'' in the case of the presence of non-orthogonality of 25% between the adjacent atomic wave functions, being computed by means of the approximate method of Brooks⁽⁶⁾. In the case of naphthalene each value of

(6) H. Brooks, *J. Chem. Phys.*, **9** (1941), 463.

Table 1.

$\alpha = 0.3$			$\alpha = 0.4$		
$-x'$	x''		$-x'$	x''	x'''
0.51728	+0.2552		0.48745	+0.2312	+0.1837
0.73243	+0.5751		0.77230	+0.6983	+0.4905
1	-0.2564		1	-0.2381	-0.1524
1	-0.4762		1	-0.5555	-0.3555
1.20736	+0.0085		1.17697	-0.0626	-0.0373
1.39765	+0.4770		1.42843	+0.6431	+0.3492
1.58274	-0.3989		1.57327	-0.5625	-0.2897
1.66759	-0.0008		1.68842	+0.0340	+0.0168
2.25520	+0.0142		2.24194	+0.0060	+0.0024
2.36492	+0.0437		2.38958	+0.0463	+0.0182
Σ ; 13.725	+0.2414		Σ ; 13.757	+0.2402	+0.2259

$\alpha = 0.8$			$\alpha = 1.0$	
$-x'$	x''	x'''	$-x'$	x''
0.38709	+0.1656	+0.1377	0.34729	+0.1442
0.92925	+2.4810	+1.6337	1	0
1	-0.1852	-0.1185	1	-0.1666
1	-1.6666	-1.0666	1	$-\infty$
1.05604	-0.8037	-0.5030	1	$-\infty$
1.54312514133	+349.0068	+181.7375	1.53209	+1.7428
1.54341698022	-348.9217	-181.6741	1.59357	-1.6544
1.80125	+0.1517	+0.0721	1.87938	+0.2176
2.19881	-0.0456	-0.0190	2.18194	-0.0983
2.51173	+0.0512	+0.0193	2.58836	+0.0509
Σ ; 13.97	+0.2335	+0.2191	Σ ; 14.122	$-\infty$

$\Sigma(x'')$ and $\Sigma(x''')$ amounts to 0.1214⁽⁴⁾ and 0.1144⁽⁶⁾ respectively. Thus, we have in Table 2 the relative anisotropies of perylene, with regard to α , taking naphthalene as a unit.

Table 2.

α	0.0	0.3	0.4	0.8	1.0
$\Delta\chi$ (perylene)/ $\Delta\chi$ (naph.)					
in orthogonal	2.0	1.99	1.97 ₈	1.92	$-\infty$
in non-orthogonal	2.0	—	1.97 ₆	1.91 ₅	$-\infty$
$\Sigma(-x')$	13.68	13.72	13.76	13.97	14.12

We can see from Table 2 that the effect of non-orthogonality is negligibly small.⁽⁷⁾

The results in Table 2 are graphically shown in Fig. 2, from which we obtain the following conclusions:

(7) cf. reference (6).

1. In case of $\alpha=1$, $\Sigma(x'')$ has no definite value.
2. The increase in value of α is accompanied by the increasing of the double bond character in $1\bar{1}$ - or $1'\bar{1}'$ -bond, and at the same

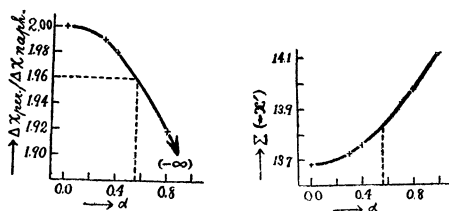


Fig. 2.

$1\bar{1}$ or $1'\bar{1}'$ being a pure single bond, the relative anisotropy is just equal to 2.0. This result is interesting; however, the alteration of the relative anisotropy with regard to α is very small except in the cases of $\alpha=0.9$ and 1.0. The experimental relative anisotropies in the preceding paper, being 1.96 and 2.02, lie within the range of $\alpha=0.0$ and 0.6.

In the special case of $\alpha=1$, as we see in Table 1, we have $x''=-\infty$ twice and $x''=0$ once, the latter representing a level which is not affected by the magnetic field. It is possible to consider that such unacceptable results may be ascribed to the quadruple roots of $x'=\pm 1$, or to the highest symmetry of the model constructed with the same, five regular hexagons. As a matter of fact, it must be true that every carbon atom in aromatic rings, in general, cannot always be the same, except in the case of benzene. Therefore, there is a sufficient reason for omitting the case of $\alpha=1$ in this problem. Moreover, it must be borne in mind that the method of molecular orbitals neglects the r_{12} repulsion effects except in so far as it is represented by the Hartree's selfconsistent field, with the result that the multiple or ionic structure occurs with an excessive probability.⁽⁸⁾ As the result of the same reason above, the $\Sigma(x')-\alpha$ curve in Fig. 2 is represented only by the attractive term wanting the repulsive one. In spite of such crudeness, the London theory is able to carry us to such a good agreement with experiment, so far from giving any discrepancy except the neighbors of $\alpha=1$.

On the other hand, however, according to Pauling's semi-classical theory, the diamagnetic anisotropy of perylene molecule has been shown to be about three times as large as that of naphthalene.⁽³⁾ As pointed out by London^{(4), (5)}, the classical theory itself may be so far from giving any

If we assume the model in Fig. 1 to be a peripheral form, in which we neglect the interactions between the π -electrons within the $10; 00'$; $01'; 1\bar{0}$; $0\bar{0}'$ and $0\bar{1}'$ bonds, we can easily derive the general formula from

(8) cf. J. H. Van Vleck, and A. Sherman, *Rev. Mod. Phys.*, **7** (1935), 170.

the London theory as follows:

$$\Delta\chi_s/\Delta\chi_{\text{Benz.}} = (6 \times n/N)^2 \times \sin \frac{\pi}{6} / \sin \frac{\pi}{N},$$

where

$$n = \frac{\text{the total area of the model in problem}}{\text{the area of benzene}},$$

and N is the number of π -electrons along the periphery. Putting $n=5$ and $N=18$, $\Delta\chi_{\text{periph.}}/\Delta\chi_B$ becomes 7.98, and in the case of $n=5$ and $N=20$, the corresponding value becomes 7.19. Both of them are far from being realized in experiment.

Summary

Applying London's theory of diamagnetic anisotropy, computations have been performed on the structure of perylene molecule. In this problem, the theory gives no definite value if we choose such a model constructed with the same, five regular hexagons as we usually do in the conventional method. Introducing a simple parameter, this difficulty is removed with the result that the relative diamagnetic anisotropy of this molecule is about twice as large as that of naphthalene, showing a good agreement with experiment. A model as a peripheral form gives a divergent result from experiment.

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**A New Method of the Colorimetric Determination
of Small Amounts of Manganese with
Silver Peroxide***

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Introduction. Small amounts of manganese can be determined accurately and quickly by the colorimetric method based upon the ease

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with which the manganese solution is oxidized to permanganate. Several oxidizing agents were proposed for this purpose by many workers. At first, lead peroxide was proposed for this purpose by Crum,⁽¹⁾ then sodium bismuthate was introduced by Reddrop and Ramage,⁽²⁾ ammonium persulfate was tried in the presence of silver ion acting as catalyst by Marshall,⁽³⁾ alkali periodate was recommended by Willard and Greathouse⁽⁴⁾ and nickel dioxide was used by Lang.⁽⁵⁾

It is well known that the excess lead dioxide or sodium bismuthate is defective in that the excess of the reagent must be removed before the comparison can be made. In the application of persulfate, it is sometimes difficult to obtain correct results⁽⁴⁾ ⁽⁶⁾, owing to the difficulty of complete oxidation. As some workers have recommended, the periodate method seems to be the best in overcoming these defects; however, it too has its handicap as it is exceedingly difficult to obtain a good quality and it is also too expensive for the routine work.⁽⁷⁾

In the persulfate method the amount of silver nitrate added is too large to consider its action simply as a catalyst. Therefore Barbier⁽⁸⁾ has proposed such an intermediate compound as $3\text{Ag}_2\text{O}_2 \cdot \text{AgNO}_3$ for the process of oxidation, while on the other hand Pinkus⁽⁹⁾ suggested the formation of silver peroxide. Although some investigators have studied this problem, none of them have been able to draw any definite conclusion.

The purpose of this investigation was therefore as follows: a) to isolate a silver compound with strong oxidizing power, b) to improve the colorimetric determination of manganese by the application of that compound.

Preparation of Silver Peroxide. On cautiously adding a slight excess of ammonium persulfate to a 10 per cent solution of silver nitrate, stirring constantly, a heavy gray precipitate is soon separated and the supernatant liquid is tinted brown. This gray precipitate is considered to be a mixture of silver peroxide and silver persulfate and the brown liquid is a nitric acid solution of silver peroxide from which silver peroxide can be precipitated when it is diluted. It is washed several times by decantation and transferred to an amber glass stoppered bottle with some water. It is desirable that this be kept in a dark cold place.

(1) W. Crum, *Lieb. Ann.*, **55** (1845), 219; R. Wasmuth, *Ang. Chem.*, **42** (1929), 133.

(2) J. Reddrop and H. Ramage, *Trans. Chem. Soc.*, **67** (1895), 268; R. O. Gortner and C. O. Rost, *Ind. Eng. Chem.*, **4** (1912), 522.

(3) H. Marshall, *Chem. News*, **83** (1901), 76; M. Dittrich, *Z. anorg. allgem. Chem.*, **80** (1913), 171; R. Lang and F. Kurtz, *Z. Anal. Chem.*, **85** (1931), 181.

(4) H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **39** (1917), 2366.

(5) R. Lang, *Z. anorg. Chem.*, **158** (1926), 370.

(6) R. O. Gortner and C. O. Rost, *Ind. Eng. Chem.*, **4** (1912), 522.

(7) H. H. Willard and J. J. Thompson, *Ind. Eng. Chem., Anal. Ed.*, **3** (1931), 399; G. J. Hough, *Ind. Eng. Chem., Anal. Ed.*, **7** (1935), 408.

(8) G. A. Barbier, *Ber.*, **60** (1927), 2424; A. Travers, *Compt. rend.*, **182** (1926), 972.

(9) A. Pinkus and L. Ramakers, *Chem. Zentr.*, **1** (1933), 1658; *Bull. Soc. Chem. Belgium*, **41** (1933), 529.

The precipitate thus obtained will be employed as a new energetic oxidizing agent and, for the sake of convenience, is called silver peroxide hereafter though it may be a mixture as mentioned above. A freshly precipitated silver peroxide may on standing undergo a change in contact with water forming a darker precipitate. It is supposed that the following reaction takes place⁽¹⁰⁾: $\text{Ag}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O}_2 + 2\text{H}_2\text{SO}_4$

When silver peroxide is added to the solution containing manganese acidified with sulfuric acid it is decomposed in a little while in the following way: $\text{Ag}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Ag}_2\text{SO}_4 + \text{H}_2\text{O} + \text{O}$

In this case the silver sulfate thus formed is a strong catalyst which decomposes hydrogen peroxide and liberates oxygen in the nascent state in the acid solution.

The oxidizing power of silver peroxide is retained for approximately half a year or more without any decrease in power as shown in Table 1.

Table 1. Oxidizing power and the duration after preparation.

Duration after preparation (days)	1	7	14	21	28	67	148
MnO found (r)	104.1	104.2	104.0	104.1	104.1	103.9	104.2

The tested solution contains 140.0 r MnO in 25 c.c. solution acidified with sulfuric acid.

Outline of Method.

A stock solution of manganese sulfate containing 0.1g. of MnO per liter is prepared by reducing potassium permanganate solution in the usual way. The standard solution of manganese containing 104.0 r of MnO used in this investigation was obtained by suitably diluting the above stock solution.

The addition of silver peroxide (name given the precipitate as aforementioned) to the acidified solution containing manganese, at room temperature and with stirring, instantaneously produces the maximum coloration due to the formation of permanganate ion. Any excess of the reagent which is left suspending in the solution is easily decomposed by warming on a water bath for 2 to 3 minutes after which the solution will be left clear. The relation between the time and temperature required for the decomposition is shown in Table 2. Though the duration after the reagent has been prepared does not reduce its oxidizing power it has been found that decomposition of excess reagent becomes quicker by long standing.

Table 2. Time required for complete decomposition at various temperatures.

days \ °C	92.5	70	60	50	40	20	10
2	3 min.	9 min.	13 min.	24 min.	45 min.	— min.	— min.
13	2	—	3	—	6	10	—
21	2	—	2	—	3	—	8

(10) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. III. p. 383, New York (1929): W. Machu, "Das Wasserstoff Peroxide und die Perverbindungen," S. 236, Wien (1937),

Through this experiment the Pulfrich photometer with filter S53 (maximum absorption 530 $m\mu$) was used. As previous workers have reported, it was found that the Lambert-Beer's law holds closely in this method.

(a) **Concentration of sulfuric acid.** The oxidation is carried out at various concentrations as shown in Table 3. Best results were obtained by using 8 to 12 per cent sulfuric acid solution. In the following experiments, a 10 per cent solution was used with a few exceptions.

Table 3. Suitable concentration of sulfuric acid.

Concentration of H_2SO_4 (%)	MnO found (r)		% of coloration*	
1	82.7	84.0	79.5	80.7
5	98.2	96.7	94.4	93.0
8	104.0	103.4	100.0	99.4
12	103.7	104.3	99.7	100.3
25	103.4	103.1	99.4	99.2
30	97.8	96.3	94.0	92.8

* % of coloration is calculated from $MnO(\text{found})/MnO(\text{calculated})$. In the above $MnO(\text{calculated})$ is 104.0 r .

(b) **Quantity of oxidizing agent.** It is convenient to handle about 0.1 to 0.15 g. (call this one unit). About 100 r MnO is oxidized sufficiently by one unit as shown in Table 4. Only two units of silver peroxide is sufficient to oxidize about 800 r manganese as MnO. If the MnO concentration is more than 10 p. p. m., the violet precipitate, presumably silver permanganate, is formed. It is, therefore, preferable to use the sample solution containing less than 10 p. p. m. of manganese as MnO.

Table 4. Amounts of silver peroxide necessary for oxidation of manganese.

Quantity (unit)	1/2		1		15		15	
MnO found (r)	90.5	93.4	104.3	103.7	104.3	104.1	104.0	104.3
Difference (r)	-13.5	-10.6	+0.3	-0.3	+0.3	+0.1	0	+0.3

The test solution contains 104.0 r manganese as MnO in 25 c.c.

(c) **Removal of excess silver peroxide.** The addition of the reagent darkens the solution. However this excess can be removed only by warming it on a water bath or by letting the solution stand for several minutes as described already. The reagent should not in any case be added to a hot solution as oxidation will no doubt be insufficient. Maximum coloration is obtained by a 2 minutes heating. Undue prolonged heating reduces the coloration.

Table 5. Differences due to heating time.

Heating time (min.)	2	4	5	7	10
MnO found (r)	104.0	103.6	102.5	97.0	77.3
Difference (r)	0	-0.4	-1.5	-7.0	-26.7

The test solution contains 104.0 r manganese as MnO in 25 c.c.

(d) **Standard curve and accuracy.** Oxidation of the various concentrations of manganese is performed in strict adherence to the condition as already established. The extinction coefficient of permanganate solution thus obtained was measured with the results shown in Table 6.

Table 6. Extinction coefficients of the solutions after oxidation of manganese by silver peroxide.

Manganese as MnO in p. p. m.	2.80	4.16	6.24	8.32
No. 1 (av. of eight readings)	0.2002	0.4039	0.6043	0.8048
No. 2 (av. of eight readings)	0.2009	0.4028	0.6034	0.8057
No. 3 (av. of eight readings)	0.2008	0.4013	0.6052	0.8059
No. 4 (av. of eight readings)	0.2018	0.4041	0.6044	0.8049
No. 5 (av. of eight readings)	0.2022	0.4017	0.6043	0.8056
Average	0.2012	0.4028	0.6037	0.8052

Filter : S53, length of the cell : 30.04 mm.

From these data the following relation between concentration and extinction coefficient is calculated by the application of least squares where X is the concentration of manganese as MnO in p. p. m. and E, the extinction coefficient of the length of 10.00 mm. cell used.

$$X = 3.439 E$$

To make sure of this relation, the extinction coefficient of permanganate solution having the same acidity was measured at various concentrations as shown in Table 7 (A). The same relation was obtained.

$$X = 3.435 E$$

It was found that results obtained by this proposed method coincide with the true value allowing for minimum difference. In other words, the accuracy of this method is proved to be satisfactory.

For purpose of comparison the potassium permanganate is treated in the same way as mentioned above (see Table 7 (B)). The following equation was obtained in the same way from the results which were cited in Table 7 (B).

$$X = 3.439 E$$

Table 7. Extinction coefficients of potassium permanganate solution when oxidation is done (B) or not (A).

MnO p. p. m.	E Exp.	A				B			
		No. 1	No. 2	No. 3	Ave.	No. 1	No. 2	No. 3	Ave.
1.992		0.1938	0.1935	0.1922	0.1932	0.1929	0.1931	0.1918	0.1926
3.984		0.3868	0.3860	0.3851	0.3859	0.3864	0.3859	0.3852	0.3858
5.976		0.5799	0.5780	0.5807	0.5795	0.5787	0.5793	0.5779	0.5786
7.968		0.7733	0.7720	0.7716	0.7723	0.7728	0.7710	0.7714	0.7717

E : Average of eight readings in one determination. Filter : S53, the length of the cell : 30.04 mm.

The results obtained correspond with the true value thus proving that silver peroxide has no obstructive effects on the process of oxidation. Thus it can be concluded from these results that silver peroxide is a superior oxidizing agent.

(c) **Reproducibility.** The following experiments were carried out to certify the accuracy of this method at various concentrations of manganese.

Table 8. Reproducibility of this method.

MnO present	MnO found (τ)					E	
						min.	max.
104.0 τ in 50 c.c.	103.4	103.8	103.7	104.3	104.5	0.2002	0.2022
104.0 τ in 25 c.c.	104.3	104.0	103.7	104.4	103.7	0.4013	0.4041
208.0 τ in 25 c.c.	207.9	208.1	208.2	207.9	208.1	0.8048	0.8059
312.0 τ in 50 c.c.	312.2	311.8	312.7	312.3	312.2	0.6034	0.6052
832.0 τ in 200 c.c.	828.5	830.4	829.5	832.2	831.0	0.4009	0.4027

E: Average of eight readings in one determination. Silver oxide: 2 units, acid concentration: 8%. Filter: S53, the length of the cell: 30.04 mm.

Thus it was proved that the proposed method may be used satisfactorily as a quick and accurate colorimetric method. Whatever difference may be caused it will be limited to 1.5 per cent.

(f) **Interference of various ions.** It is necessary to study the interference of various ions as the oxidizing agent used here has been newly tried.

The interference ions are divided into three groups: 1) colorless ions, 2) colored ions, 3) ions precipitated by silver, sulfate ions or in acid solution.

(1) Colorless ions. Some colorless ions do not interfere with the colorimetric determination of manganese as would be expected. As a large quantity of ferric ion interferes with the coloration of the permanganate, the addition of phosphoric acid is necessary to prevent this interference. Some reducing ions, namely ferrous, sulfite, nitrite, oxalate, tartrate and other oxidizable organic anions in small amounts can be easily oxidized with further addition of silver peroxide. White silver sulfate will sometimes precipitate. In this case it is desirable to reoxidize after filtering off. If a large amount of such ions is present, it is safer to remove or destroy the ions by evaporation with nitric acid or a mixture of nitric acid and sulfuric acid before the oxidation is carried out. (see Table 9).

(2) Colored ions. Some interferences are expected when the colored ions are present in the sample solution. However the effect of some of these may be compensated by the use of an aliquot portion or by the addition of the same amount in the reference cell of photometer as shown in Table 10.

As the above tests have indicated there is no obstacle met by the presence of these ions especially chromium, titanium, up to the above concentration in the application of this new reagent. None of these interferences need be considered because the cited ions can be easily separated by the usual method.

(3) Ions precipitated by silver ion, sulfate ion or in acid solution. Chloride precipitates by a slight excess of silver nitrate. However it is preferable to remove it by evaporation with sulfuric acid. Other ions may be removed simply by filtration with no serious effects as shown in Table 11.

Proposed Method. As already described it is proved that the colorimetric determination of manganese may be successfully performed by utilizing the new oxidizing agent. The general procedure will be des-

Table 9. Ions which have no interfering effect.

Ions	Salt used	Amount present (against 104.07 MnO) (mg.)		MnO found (r)	Difference (r)
Al ⁺⁺⁺	Al ₂ (SO ₄) ₃	Al	100 (1:1000)	103.8	-0.2
As ⁺⁺⁺	As ₂ O ₃	As ₂ O ₃	100 (1:100)	103.8	-0.2
NH ₄ ⁺	(NH ₄) ₂ SO ₄	NH ₄	100 (1:1000)	103.8	-0.2
Bi ⁺⁺⁺	Bi(NO ₃) ₃	Bi	10 (1:100)	104.0	0
Ca ⁺⁺	Ca(NO ₃) ₂	Ca	10 (1:100)	104.0	0
Cd ⁺⁺	Cd(NO ₃) ₂	Cd	100 (1:1000)	103.6	-0.4
Fe ⁺⁺⁺	Fe(NO ₃) ₂	Fe	100 (1:1000)	104.0	0
Mg ⁺⁺	MgSO ₄	Mg	100 (1:1000)	103.4	-0.6
Sn ⁺⁺⁺	Sn(SO ₂) ₄	Sn	100 (1:1000)	103.9	-0.1
Tl ⁺	Tl ₂ SO ₄	Tl	10 (1:100)	103.3	-0.7
Zn ⁺⁺	ZnSO ₄	Zn	100 (1:1000)	103.6	-0.4
VO ₃ ⁻	NH ₄ VO ₃	V ₂ O ₃	10 (1:100)	104.2	+0.2
BO ₂ ⁻	Na ₂ B ₄ O ₇	B ₂ O ₃	100 (1:1000)	103.7	-0.3
MoO ₄ ⁻⁻	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	MoO ₃	140 (1:1400)	104.2	+0.2
PO ₄ ⁻⁻⁻	Na ₂ HPO ₄	P ₂ O ₅	1000 (1:10000)	104.0	0
SiO ₃ ⁻⁻	Na ₂ SiO ₃	SiO ₂	5 (1:50)	104.1	+0.1
F ⁻	NaF	F	0.16 (1:1.6)	104.0	0
NO ₃ ⁻	HNO ₃	NO ₃	2.8 (1:28000)	104.0	0
PO ₄ ⁻⁻⁻	H ₃ PO ₄	P ₂ O ₅	1500 (1:15000)	104.4	+0.4
C ₂ O ₄ ⁻⁻	(COONa) ₂	C ₂ O ₄	14 (1:140)	104.2	+0.2
C ₄ H ₄ O ₆ ⁻⁻	NaKC ₄ H ₄ O ₆	C ₄ H ₄ O ₆	5 (1:50)	103.8	-0.2

Table 10. Colored ions.

Ions	Salt used	Amount present (against 104.07)(mg.)		MnO found (r)	Difference. (r)	Remarks
Cr ⁺⁺⁺	Chrom-alum	Cr	10 (1:100)	103.2	-0.8	after oxidation with Na ₂ O ₂
Cr ₂ O ₇ ⁻⁻	K ₂ CrO ₄	Cr	10 (1:100)	104.1	+0.1	
Cu ⁺⁺	CuSO ₄	Cu	100 (1:1000)	104.2	+0.2	isolated as CuS
Cu ⁺⁺	CuSO ₄	Cu	100 (1:1000)	104.3	+0.3	
Nd ⁺⁺⁺	Nd(NO ₃) ₃	Nd ₂ O ₃	50 (1:500)	104.6	+0.6	acid concentration 25 %
Ni ⁺⁺	NiSO ₄	Ni	50 (1:500)	104.5	+0.5	
Ti ⁺⁺⁺	Ti(OH) ₄	TiO ₂	10 (1:100)	104.0	0	added 10 units
rare earths	nitrate	about	50 (1:500)	103.8	-0.2	Nd(NO ₃) ₃ containing other rare earths
Co ⁺⁺	CoSO ₄	Co	10 (1:100)	104.3	+0.3	the comparison solu- tion must be treated as a sample with sil- ver peroxide

cribed below. If the sample contains a large amount of chloride add sulfuric acid and evaporate until fumes of the latter appear. If the amount of chloride is small it may be separated as silver chloride.

Table 11. Ions precipitated in the procedure.

Ions	Salt used	Amount present against 104.0 γ (mg.)	MnO found (γ)	Difference (γ)	Remarks
Ba ⁺⁺	Ba(NO ₃) ₂	Ba 100 (1:1000)	104.6	+0.6	
Sr ⁺⁺	Sr(NO ₃) ₂	Sr 100 (1:1000)	104.0	0	
Hg ₂ ⁺⁺	Hg ₂ (NO ₃) ₂	Hg 100 (1:1000)	103.8	-0.2	
Cl ⁻	NaCl	Cl 100 (1:1000)	103.8	-0.2	
Pb ⁺⁺	Pb(NO ₃) ₂	Pb 100 (1:1000)	104.0	0	
Ca ⁺⁺	Ca(NO ₃) ₂	Ca 100 (1:1000)	103.7	-0.3	alcohol added to decrease the solubility
Ca ⁺⁺	Ca(NO ₃) ₂	Ca 50 (1:500)	104.1	+0.1	isolated as oxalate
SiO ₃ ⁻⁻	Na ₂ SiO ₃	SiO ₂ 100 (1:1000)	103.8	-0.2	separated as insoluble SiO ₂
SiO ₃ ⁻⁻	Na ₂ SiO ₃	SiO ₂ 100 (1:1000)	104.3	+0.3	SiO ₂ filtered off after treating with H ₂ SO ₄
WO ₄ ⁻⁻	Na ₂ WO ₄	W 100 (1:1000)	104.1	+0.1	digested with HNO ₃ and filtered

In the presence of a large quantity of ferrous ion and other oxidizable substance, boil with nitric acid or add the later before evaporating with sulfuric acid. The best method for the separation of chromium involves oxidation in basic solution as many workers have recommended, whereby manganese is precipitated with iron, titanium and others. In like manner other undesirable matter can be easily separated from manganese with no interfering effects.

It is most convenient to apply hydroxide precipitation method with a little ferric salt as a collector to concentrate very small amounts of manganese as in the case of natural water (as little as 10 γ per liter). The sample solution thus obtained ready for colorimetric determination should contain 10 per cent of sulfuric acid in the final step. Then add about 0.1 g. silver peroxide stirring constantly. Heat on water bath for 2 minutes or let stand for several minutes to obtain the maximum coloration of the manganese. Dilute to the definite volume and make the color comparison in any convenient way.

By this method as little as 1 p.p.m. of manganese (as MnO) can be easily determined with the best results. This method was retested by determining manganese in natural water, hot springs water and biological materials, results of which will be given in a latter communication.

Summary

In face of several defects noted by the oxidation agents hitherto used in the determination of manganese by the colorimetric method a new reagent, so-called "Silver peroxide," has been proposed. This new reagent

has been found to excel other reagents in the following respects: a) easy preparation and easy decomposition of the excess reagent, b) strong oxidizing power not reduced by long standing and cheap availability for routine work, c) no noticeable interference by other reagents during action and accuracy in results obtained.

Thus by its use the procedure is exceedingly simplified and the time required is considerably less than that in the method used hitherto.

The author wishes to express his sincere appreciation to Professor Kenjiro Kimura for his valuable suggestion and his never-failing encouragement during this investigation. He is also grateful to Mr. M. Tanaka for his helpful advice and sincere friendship which facilitated this work.

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The Theory of the Rubber-like Elasticity in Monolayers.⁽¹⁾

By Keizō SUZUKI.

(Received February 1, 1949.)

Introduction. When a monolayer is made from high-molecular compound with rubber-like elasticity, what are its properties?

We succeeded in making a monolayer by dropping the benzene solution of the addition polymer of butadiene with acrylonitrile onto the water surface, and measured the surface pressure changing the surface area and temperature⁽²⁾ (Fig. 1). The monolayer takes the most extended form under no external force. On the contrary the three-dimensional rubber block set free assumes the most contracted form as well known. A thin rubber layer on water which has a similar nature to the three-dimensional one was studied by Trapeznikov,⁽³⁾ but it is too thick to be called a monolayer.

This difference between the two states of the substances seems, at first sight, to be a serious hindrance for us to find common properties in them. But we find the expression of the rubber-like elasticity in the two

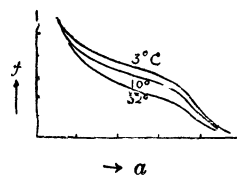


Fig. 1.

Fig. 1. The surface pressure and the surface area of the monolayer of addition polymer of butadiene 5 and acrylonitrile 2.

(1) Short abstract of the mathematical part is already reported in Japanese. K. Suzuki and Y. Suzuki, *Kagaku*, **17** (1947), 238.

(2) K. Suzuki, *J. Chem. Soc. Japan*, **63** (1942), 1058.

(3) A. A. Trapeznikov, *Compt. rend. U. R. S. S.*, **95** (1941), 138.

properties of the monolayer: extraordinarily large and reversible compressibility over a wide range of the area, and the decrease of the surface area and surface pressure with increasing temperature.

The Structure of the Monolayer. Can all the substances with rubber-like elasticity spread to monolayers? No; for example, natural cauchouc can never spread to the monolayer on water, for it has no "hydrophilic groups". The monolayer on water, generally speaking, can be formed only by the partially hydrophobic and partially hydrophilic molecules.⁽⁴⁾ High polymeric molecules with hydrophobic backbones must have hydrophilic radicals to spread to monolayers; our sample has the nitrile groups. Another sample with phenyl radicals instead of nitriles failed to spread.

The hydrophilic radicals, which take the states of lower energy by attaching to water, tend to spread the molecule broader and thinner on the water surface, and on the other hand the thermal motion of the molecular chains tends to contract to the more coiled and gathered forms, the more probable state, like the three-dimensional case. The balance of the two forces appears to us as the properties of the monolayer above shown. The elevation of temperature increases the thermal motion and contracts the area of the film.

As long as we call the spontaneous contraction of the long chain molecule by thermal motion as the rubber-like elasticity,⁽⁵⁾ we must regard the nature of this monolayer as an expression of the same sort of elasticity. The statistical treatment on the elasticity has had successful results. We shall now try a statistical evaluation of the mechanical and thermodynamical properties of the monolayer.

We must set up a model which fits this monolayer.

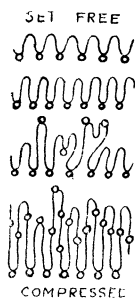


Fig. 2:

Fig. 2. The schema
compression.

The observed nature does not permit the simple translation of the finely constructed three-dimensional theory to the two-dimensional one. Our model must be able to bear under the reversible compression to the fairly thick layer which may irreversibly destroy the monolayers of low molecular compounds. By this compression some parts of our molecule are pushed up from the water surface but they are ready to return to the water surface by the release from the compression (Fig. 2). This is the reason why the two-dimensional model cannot be adopted for our monolayer, although it was recently applied for some polymeric monolayer of the expanded type by Singer.⁽⁶⁾

Probability for Configurations of the Chain. We consider a long chain molecule with n hydrophilic groups in equal intervals. Let the intervals be m -membered chains, then the molecule is mn -membered

(4) N. K. Adam, "The Physics and Chemistry of Surfaces," (Oxford 1941), Chapt. II.

(5) W. Kuhn, *Kolloid-Z.*, **86** (1936), 258; H. Dostal, *Mh. Chem.*, **71** (1938), 144; F. Horst Müller, *Kolloid-Z.*, **95** (1941), 133; R. Kubo, *Proc. Phys. Soc. Japan*, **2** (1947), 51.

(6) S. J. Singer, *J. Chem. Phys.*, **16** (1948), 842.

($n \geq 1$) (Fig. 3).

We shall estimate the probability W_{an} that an hydrophilic groups are in contact with water surface and $(1-a)$ n groups are not. For a while we put the energy difference due to the hydration out of consideration. Let u_i be the probability that when a certain group is on water the i -th group from it is on water and the intervening $i-1$ groups are not.

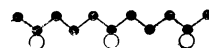


Fig. 3.

Fig. 3. The linear molecule.

Then the probability that the chain takes the configuration in Fig. 4 is $u_3 u_2 u_1 u_1$. Generally it becomes the product of $a n u_i$'s, where the sum of i 's becomes n . The number of selection of an groups is ${}_n C_{an}$, then the probability W_{an} is the sum of ${}_n C_{an}$ products similar to the product above shown:

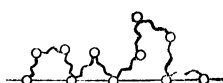


Fig. 4.

Fig. 4. A schematic configuration.

$$W_{an} = \sum {}_n C_{an} \prod u_i. \quad (1)$$

This is obtained as the factor of x^n of $(\sum_i u_i x^i)^{an}$:

$$\sum_n W_{an} x^n = (\sum_i u_i x^i)^{an}. \quad (2)$$

Next we rewrite u_i in the calculable form. Let p_i be the probability that when a certain group is on water the i -th group from it is on water too. p_i contains, contrary to u_i the cases that some of the $i-1$ intervening groups are on water. p_0 is the probability that when a group is on water the same group is on water, therefore

$$p_0 = 1.$$

p_1 is the probability that the next group is on water. In this case there is no intervening group, therefore

$$p_1 = u_1.$$

p_2 is the probability that the second group is on water, and is the sum of two cases: the case where the intervening group is on water and the case that it is not. The probabilities are

$$u_1 u_1 \text{ or } u_1 p_1, \quad u_2 \text{ or } u_2 p_0$$

respectively. And then we have

$$p_2 = u_1 p_1 + u_2 p_0.$$

Similarly p_3 is separated into three cases and

$$p_3 = u_1 p_2 + u_2 p_1 + u_3 p_0$$

is obtained. Generally p_j is separated into j terms: the first group is on

water = $u_1 p_{j-1}$, the second group is on water = $u_2 p_{j-2}$, and the i -th group is on water = $u_i p_{i-j}$. Then

$$p_j = \sum_{i=1}^j u_i p_{j-i}. \quad (3)$$

These lead to the equation:

$$p_1 x + p_2 x^2 + \dots = (p_0 + p_1 x + \dots) (u_1 x + u_2 x^2 + \dots),$$

which gives the mother function of u_i by a transformation:

$$\sum_{i=1}^{\infty} u_i x^i = \sum_{i=1}^{\infty} p_i x^i / \sum_{i=0}^{\infty} p_i x^i. \quad (4)$$

Putting this in (2), we have

$$\sum_n W_{\alpha n} x^n = \left(\sum_{i=1}^{\infty} p_i x^i / \sum_{i=0}^{\infty} p_i x^i \right)^{\alpha n} \quad (5)$$

We shall now consider how p_i 's be expressed. p_i is the probability that when an end of the im -membered chain is on water another end is also on water.

The Brownian movement gives a good analogy. Let us estimate the probability that a particle which started from a planar wall at time 0 comes back to and collides with the wall at time im . Let the wall be the plane $z=0$. We compare two sorts of traces of the particle which was on $z=0$ at $t=0$: one where the wall is perfectly elastic and the other where there is no wall. The traces of the former are obtained from those of the latter by folding the one half on the side of the negative z on to the other half (Fig. 5).

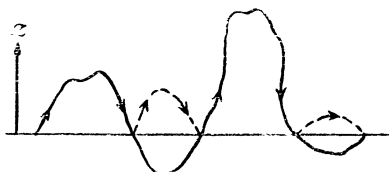


Fig. 5.

Fig. 5. A trace of a Brownian particle about an elastic wall.

Therefore the probability that the particle of the first kind passes through the plane $z=0$ in the time interval $t \sim t+dt$ equals the probability that the particle of the second collides in the same time.

Similarly p_i is obtained as the probability that when an end of the im -membered chain is on the plane $z=0$ another end is also on the plane.

Here the plane is not a wall nor a water surface but an imagined geometrical surface.

Thus p_i can be known from the degree of flexibility of the chain. The more flexible the chain, the larger becomes p_i .

The estimation of p_i is perfectly mathematical on the simple chain, each unit of which has equal probability, $1/2$, to take $+1$ or -1 as the z -component of its length:

$$p_0 = 1, \quad p_1 = {}_m C_{m/2} 2^{-m}, \quad p_2 = {}_{2m} C_m 2^{-2m},$$

$$p_i = {}_{im} C_{im/2} 2^{-im} \cong (\pi m/2)^{-0.5} i^{-0.5}.$$

If im is not so small, p_i is generally approximated as

$$p_0 = 1, \quad p_i = B i^{-0.5} \quad \text{for } i > 1, \quad (6)$$

where B is a constant proportional to the reciprocal square root of m , for the distribution of the relative position of the two ends of a chain is well approximated by the Gaussian distribution.^{(1),(7)}

Putting $i=1$ in (6), we have $B=p_1$. B is the probability that when one end of m -membered chain is on water the other is also on it. This probability must be proportional to the square root of m , and the proportional constant can be known from the nature of the chain, from the pseudosegment⁽⁸⁾ expressing the flexibility and the width of the potential valley at the surface of water for the hydrophilic group. A further estimation is deferred to another paper and here only the qualitative conclusion is stated: the more flexible chains with hydrophilic radicals in shorter intervals have larger values of B .

Surface Pressure. Statistical thermodynamics tells us the equation

$$fnda = -kTd \log Z_{an}, \quad (7)$$

where f is the surface pressure, a is the surface area per radical, and Z_{an} is the partition function. $fnda$ is the work done by the molecule with the increase of area nda , so it is equal to the decrease of the free energy $-kTd \log Z_{an}$.

We have neglected the energy due to the hydration of hydrophilic groups in the calculation of W_{an} . Therefore the partition function is substituted by W_{an} multiplied by $\exp(-\epsilon an/kT)$, in which ϵ is the hydration energy of a group k is the Boltzmann's constant, and T is absolute temperature. Then the equation (7) gives

$$f = \left(\epsilon + \frac{kT}{n} \frac{d}{da} \log W_{an} \right) \frac{da}{da}. \quad (8)$$

The differential calculus in the bracket is carried by the use of the mother function of W_{an} (5):

$$W_{an} = \frac{1}{2\pi\lambda} \oint \frac{dx}{x^{\lambda+1}} \left(\sum_{i=1}^{\infty} p_i x^i \middle/ \sum_{i=0}^{\infty} p_i x^i \right)^{an},$$

where λ is $\sqrt{-1}$, i in the ordinary notation. Approximation at the saddle point leads to

(7) S. Chandrasekhar, *Rev. Mod. Phys.*, **15** (1943), 3~16.

(8) K. Suzuki, this Bulletin, **20** (1947), 19.

$$W_{an} = x^{-n} \left(\sum_{i=1}^{\infty} p_i x^i / \sum_{i=0}^{\infty} p_i x^i \right)^{an} \dots, \\ \frac{d}{da} \log W_{an} = n \log \left(\sum_{i=1}^{\infty} p_i x^i / \sum_{i=0}^{\infty} p_i x^i \right), \quad (9)$$

in which x is the value corresponding to the extreme value of the integrand in the course of the integration. x is given by the equation

$$\alpha = \sum_{i=1}^{\infty} p_i x^i \sum_{i=0}^{\infty} p_i x^i / \sum_{i=1}^{\infty} i p_i x^i, \quad (10)$$

which is obtained by equating the differential coefficient of the logarithm of the integrand to zero. Inserting (9) in (8) one obtains

$$f = \left\{ \varepsilon + kT \log \left(\sum_{i=1}^{\infty} p_i x^i / \sum_{i=0}^{\infty} p_i x^i \right) \right\} da/da, \quad (11)$$

in which x is given by (10). The use of (6) for p_i in (10) and (11) yields

$$f = \left[\varepsilon - kT \log \left\{ \left(B \sum_{i=1}^{\infty} i^{-0.5} x^i \right)^{-1} + 1 \right\} \right] da/da, \quad (12)^{(9)}$$

$$\alpha = \sum_{i=1}^{\infty} i^{-0.5} x^i \left(1 + B \sum_{i=1}^{\infty} i^{-0.5} x^i \right) / \sum_{i=1}^{\infty} i^{0.5} x^i. \quad (13)^{(9)}$$

Surface pressure is independent of molecular weight or polymerization degree n , but depends only on the hydrophilicity ε of the groups and

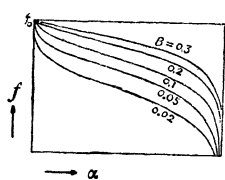


Fig. 6.

Fig. 6. Calculated Relations of f with α .

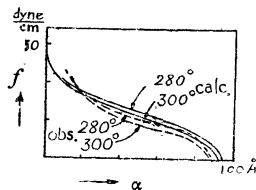


Fig. 7.

Fig. 7. Comparison of theory and observation. Calc.: $B = 0.02$, $da/da = 100 \text{ Å}^2$, $\varepsilon = 3.10^{-13} \text{ erg}$. Obs.: polymer from butadiene 5 and acrylonitrile 1.

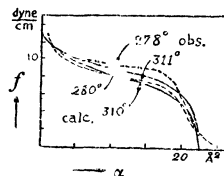


Fig. 8.

Fig. 8. Comparison of theory and observation. Calc.: $B = 0.1$, $da/da = 23 \text{ Å}^2$, $\varepsilon = 1.3 \cdot 10^{-13} \text{ erg}$. Obs.: polymethylsiloxane.

the flexibility B of the m -membered chain.

The Numerical Results. Calculated relations of f with α are

(9) The numerical summations of the series in (12) and (13) are carried by the equations:

$$\sum i^{0.5} x^i = \frac{\sqrt{\pi}}{2} \{ (1-x)^{-1.5} - x \} + \sum \left(i^{0.5} - \frac{\sqrt{\pi}}{2} \cdot \frac{3}{2} \cdot \frac{5}{4} \dots \frac{2i-1}{2i-2} \right) x^i,$$

$$\sum i^{-0.5} x^i = \sqrt{\pi} \{ (1-x)^{-0.5} - 1 \} + \sum \left(i^{-0.5} - \frac{\sqrt{\pi}}{2} \cdot \frac{3}{4} \cdot \frac{5}{6} \dots \frac{2i-1}{2i} \right) x^i.$$

plotted in Fig. 6 assuming the constant ϵ , T , and da/da . If the energy s becomes large f_0 becomes large and the curves move upwards conserving the forms. If the temperature becomes high, f_0-f becomes large proportionally to T . ($f_0=\epsilon da/da$).

Experimental curves are compared with the theoretical ones in Fig. 7. The monolayer of polymethylsiloxane in Fig. 8 studied by Fox, Taylor, and Zisman⁽¹⁰⁾ fits the larger B , for the molecule has more consecutive hydrophilic parts. They assume a particular structure, the helix form of the chain, but such a somewhat regular structure may not explain the temperature effect. It is necessary that the compression increases the entropy. The constant surface potential over the wide range of compression observed by Fox *et.al.* shows the validity of the assumption of constant da/da ; because the constant da/da means the constant number of oriented radicals per area, and only the oriented ones are effective to surface potential, for the moments of the others take random directions and cancel each other.

Conclusion. It is a destined difficulty in the problem of the rubber elasticity what kind of macroscopic variable is combined with the microscopic thermal motion, since Kuhn assumed that the relative movement of the two ends of the chain is proportional to the macroscopic transformation.

In this theory the surface area is reasonably combined with the number of hydrated hydrophilic groups.

The second difficulty is the interaction of molecules, which is usually neglected and in this theory too. But we may expect the effect of the negligence to be smaller in the monolayer, because the chains are set more free from each other in it than in the three-dimensionally filled cases.

Thus the theory of the statistical elasticity seems to find the first step for its quantitative explanation.

Summary.

A discussion is made on the structure of the monolayer of the rubber-like highpolymer, and the equation of state is derived from the statistical theory. The extraordinarily large compressibility and the inverse temperature effect observed in the experiment are explained to be the expressions of the rubber-like elasticity. The theory is not a simple translation of the 3-dimensional theory to the 2-dimensional one.

The author wishes to express his sincere thanks to Yasutaka Suzuki for his remarkable contribution on the mathematical parts of this work.

*Masaoka-cho, Toyokawa, Aichi pref.,
Japan.*

(10) H. W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **39** (1947), 1401.
They also found the gradual metamorphosis of the rubber monolayer into the expanded film, which we reported in (2).

Über den Reaktionsmechanismus der Dianthracenbildung aus Anthracen. II.

Von Momotaro SUZUKI.

(Eingegangen am 1. Februar 1949.)

In einer früheren Mitteilung⁽¹⁾ haben wir die folgenden Ergebnisse über die Photopolymerisation des Anthracens ins Dianthracen berichtet.

1. Bei kleinerer Anfangskonzentration des Anthracens nimmt die Menge des gebildeten Dianthracens mit der Konzentration zu. Wir wollen dieses Konzentrationsgebiet hier Gebiet A nennen.

2. Oberhalb eines bestimmten A_0 der Anthracenkonzentration ist die Menge des gebildeten Dianthracens unabhängig von der Konzentration des Anthracens. Dieses Gebiet nennen wir Gebiet B und in der früheren Arbeit hat es sich hauptsächlich um den Reaktionsmechanismus in diesem Gebiet gehandelt. Ein Mechanismusschema ist vorgeschlagen, womit erklärt werden soll, dass diese Umsetzung trotz bimolekularer Bildungsweise eine Art von nullter Ordnung aufweist. Man hat übrigens die gute Übereinstimmung der Versuchsergebnisse mit der angenommenen Postulation festgestellt.

In dem vorliegenden Teil sollen dieselben durch einige Versuche ergänzt werden, welche zu bestimmen, später näher zu diskutierenden Zwecken ausgeführt wurden. Alsdann haben wir den Messbereich der Konzentrationen des Anthracens sowie die Versuchstemperaturen noch weiter variiert, den experimentellen Befund zu prüfen und zu untersuchen, ob er sich mit dem vorgeschlagenen Reaktionsschema und den davon abhängenden Postulationen erklären lässt.

Versuchsanordnung und Durchführung. Die Versuchsanordnung und Durchführung der Versuche waren die gleiche, wie wir sie bereits in der vorigen Mitteilung beschrieben haben. Es kann wegen aller Einzelheiten derselben auf die dort gegebene Beschreibung verwiesen werden. Nur einige Kleinigkeiten waren geändert; und zwar die Umgebungstemperatur der Quecksilberbogenlampe, die als Lichtquelle diente, konstant zu erhalten, um die Lichtintensität des ins Reaktionsgefäß einfallenden Lichtes noch genauer konstant erhalten zu können.

Die Anfangskonzentration des Anthracens wurde noch weiter verändert und die Messung bei drei Temperaturen, d.i. -10° , 0° und 30° durchgeführt.

Die Reinigung der Materialien geschah auch in genau gleicher Weise wie beim vorigen Versuch.

Messresultate. In der Tabelle 1, sowie auch in Fig. 1 sind die Versuchsergebnisse aufgezeichnet. Bei den Kurven in der Figur ist die in einer bestimmten Belichtungszeit, und zwar in 7.0 sowie auch 5.0 Stunden

(1) M. Suzuki, I. Mitteilung, dies Bulletin, **18** (1943), 146.

gebildete Menge des Dianthracens bei verschiedener Reaktionstemperatur gegen die Anfangskonzentration des Anthracens aufgetragen. Die linken Teile der Kurven zeigen genau dieselben Verläufe wie in Fig. 5 der vorigen Mitteilung. Wir sehen aber beim höheren Konzentrationsgebiet, dass noch eine andere Art Reaktionsverlauf vorhanden ist, bei dem die Menge des gebildeten Dianthracens wieder mit der Anfangskonzentration des Anthracens zunimmt und zwar ungefähr linear. Wir wollen dieses Gebiet C nennen. In diesem Gebiet C nimmt die Reaktionsgeschwindigkeit der Dianthracenbildung plötzlich und beträchtlich mit der Anfangskonzentration des Substrats zu. Übrigens steigt die gebildete Menge des Dianthracens in einem bestimmten Zeitintervall in diesem Gebiet mit der Temperatur viel stärker an als beim Gebiet B.

In diesen drei vereinzelteten Teilen bildet sich das Dianthracen aus Anthracen durch den je nachdem verschiedenen Reaktionsmechanismus.

In Tabelle 2 und Fig. 2 zeigen sich wieder die Verläufe der Beziehungen zwischen der gebildeten Menge des Dianthracens und der Anfangskonzentration des Anthracens bei gleichen Temperaturen und mit verschiedener Belichtungszeitdauer, und zwar nämlich 5.0, 7.0 und 10.0 Stunden. Dabei verhalten sich die Kurven fast analog wie in Fig. 1.

Übrigens haben wir die Messung der Quantenausbeute im Gebiet B unter Benutzung von 366μ monochromatischem Licht vorgenommen. Die Ergebnisse sind in folgendem Abschnitt angegeben.

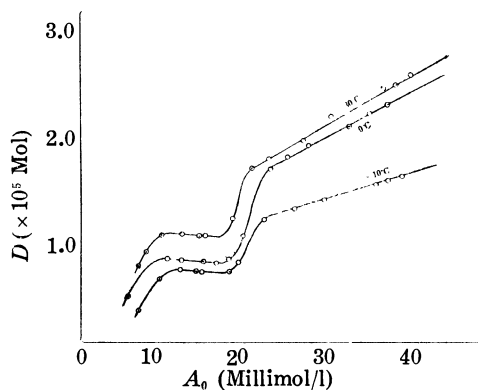


Fig. 1 (b) 5.0 Stunde Belichtung.

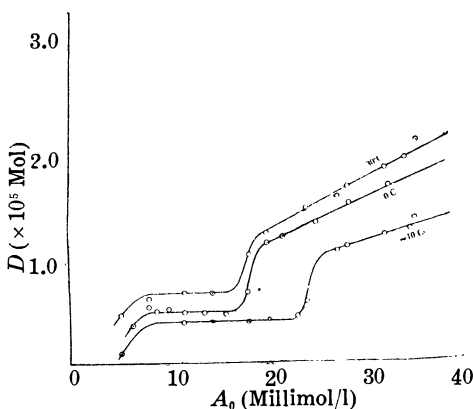


Fig. 1 (a) 7.0 Stunde Belichtung.

Quantenausbeute und Aktivierungsenergie. Die Quantenausbeute dieser Umsetzung im Gebiet B mit dem monochromatischen Licht von 366μ ist folgenderweise zu bestimmen. Die gebildete Menge des Dianthracens in einer bestimmten Belichtungszeitdauer lässt sich durch die Umsatzmenge des Anthracens pro Zeiteinheit berechnen. Die Lichtmenge aus

der monochromatischen Lichtquelle kann man durch die Forbeslösung⁽²⁾ bestimmen, nachdem man die mit KMnO_4 -Lösung titriert hatte.

(2) Leighton und Forbes, J. Am. Chem. Soc., 52 (1930), 3191.

Tabelle 1.

Die Menge des gebildeten Dianthracens aus der Anthracen-
lösung mit verschiedenen Anfangskonzentrationen.

Versuchstemperatur -10°C , 0°C und 30°C
Belichtungsdauer 7.0 Stunden

-10°C		0°C		30°C	
A_0	D	A_0	D	A_0	D
8.5	0.146	7.20	0.281	8.5	0.758
10.5	0.487	8.12	0.618	10.1	0.927
12.2	0.609	10.8	0.703	12.1	0.954
13.8	0.590	12.3	0.699	13.8	0.954
14.5	0.590	14.5	0.704	14.5	0.963
17.2	0.609	15.7	0.703	17.2	1.18
18.1	0.730	17.0	0.752	18.6	1.69
20.2	1.18	18.3	1.00	20.2	1.80
23.2	1.32	20.4	1.70	23.4	2.02
26.1	1.43	22.0	1.83	26.1	2.19
31.2	1.63	24.0	1.98	31.2	2.61
32.4	1.69	27.9	2.19	32.4	2.67
33.7	1.74	31.7	2.46	33.7	2.78

Belichtungsdauer 5.0 Stunden.

-10°C		0°C		30°C	
A_0	D	A_0	D	A_0	D
5.2	0.100	6.4	0.380	5.2	0.480
8.0	0.560	8.8	0.520	8.0	0.640
11.7	0.410	10.0	0.532	11.7	0.702
14.4	0.405	11.7	0.500	14.4	0.690
18.2	0.412	13.6	0.502	18.2	1.08
20.2	0.430	15.7	0.490	20.0	1.31
24.0	0.604	18.1	0.701	24.0	1.56
27.2	1.12	20.0	1.21	27.2	1.66
28.2	1.17	21.7	1.26	28.2	1.76
32.0	1.29	25.1	1.41	32.0	1.96
34.6	1.34	28.3	1.60	34.0	2.06
35.1	1.44	32.4	1.78	35.1	2.44

A_0 : Anfangskonzentration des Anthracens in Toluollösung in Millimol
pro Liter.

D : Gebildete Menge des Dianthracens in 10^{-5} Mol.

Um über die Lichtabsorption der untersuchten Lösungen in verschiedenen Schichtdicken sowie auch über die Forbeslösung nähere Kenntnis zu erlangen, wurden die Messungen der Durchlässigkeit der genannten Flüssigkeit durchgeführt. Zu diesem Zwecke diente ein Photometer aus einer Vakuumphotozelle mit Innenschlag von Kalium mit Anschluss eines einstufigen Röhrenverstärkers. Um das Versuchsgefäß immer in gleicher Lage zu halten, wurde es in einen kleinen mit geeigneten Ausschnitten versehenen Aluminiumblock eingeschoben, in dem es durch ein Feder immer in gleicher Weise festgehalten wurde, mit Filter und Linsensystem versehene Beleuchtungslampe und das eigentliche Gehäuse der Photozelle

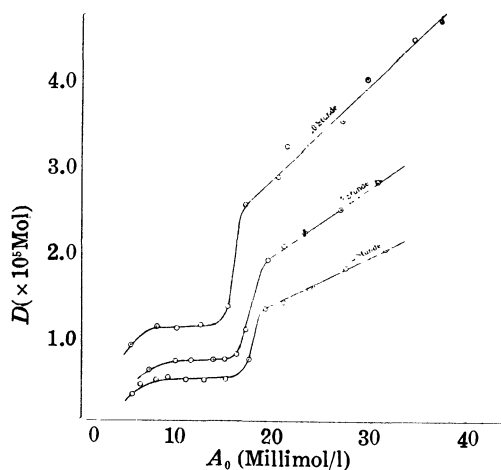


Fig. 2.

Tabelle 2.

Die Menge des gebildeten Dianthracens aus der Anthracenlösung in Toluol mit verschiedenen Anfangskonzentrationen und bei verschiedenen Belichtungszeitdauern.

Versuchstemperatur 0°C

5.0 Stunden.		7.0 Stunden.		10.0 Stunden.	
A_0	D	A_0	D	A_0	D
6.4	0.380	7.20	0.481	6.3	0.871
8.8	0.520	8.12	0.618	9.0	1.06
10.0	0.532	10.8	0.703	10.8	1.04
11.7	0.500	12.3	0.699	13.4	1.06
13.6	0.502	14.5	0.704	16.2	1.14
15.7	0.499	15.7	0.703	18.2	2.25
18.1	0.701	17.0	0.752	22.5	2.86
20.0	1.21	18.0	1.00	28.4	3.10
21.7	1.26	20.4	1.70	30.8	3.52
25.1	1.41	22.0	1.83	35.9	3.91
28.3	1.60	24.0	1.98	38.8	4.08
32.4	1.78	27.9	2.19		
		31.7	2.46		

A_0 : Anfangskonzentration des Anthracens in Toluollösung in Millimol pro Liter.

D : Gebildete Menge des Dianthracens in 10^{-5} Mol.

eingesetzt. Das Versuchsgefäß stand hierbei senkrecht, die Schichtdicke der durchstrahlten Lösung wurde genau abgelesen. Die gute Übereinstimmung wiederholter Messungen bewies die Reproduzierbarkeit dieser Aufstellung. Auf diese Weise konnte man das Absorptionsvermögen der Anthracenlösung sowie auch der Forbeslösung bei den verschiedenen Schichtdicken und auch bei verschiedenen Konzentrationen bestimmen. Das Absorptionsvermögen der Anthracenlösung nimmt bei der kleinen Schichtdicke mit Zunahme derselben zu, aber es nimmt bald einen konstanten Wert an und unter unseren Versuchsbedingungen behält es durchaus seinen konstanten Wert der bei der ein wenig schwankenden Schichtdicke nicht wesentlich variiert.

Aus dem Versuche ging hervor, dass das Verhältnis der Lichtabsorption der Forbeslösung und die Anthracenlösung unter unseren Versuchsbedingungen den Wert 2.45 aufwies. Daraus kann man die Zahl J von der Anthracenlösung absorbierten Lichtquanten von 366μ pro Sek. berechnen. Wir haben als den Zahlenwert von $J=2.66 \times 10^{15}$. Das Verhältnis der in einer Sekunde gebildeten Dianthracenmolekülen D und der absorbierten Lichtquantenzahl J , also die Quantenausbeute bei verschiedenen Temperaturen ersieht man aus Tabelle 3. Dabei nimmt man als Zahlenwert der Quantenausbeute von der Forbeslösung 0.457 und wegen seines kleinen Temperaturkoeffizienten haben wir die Veränderung des oben geschriebenen Wertes mit der Temperatur ohne weiteres nachgelassen. Die Beleuchtung dauerte dabei immer 7.0 Stunden.

Nun können wir die von uns gewonnenen Zahlenwerte der Quantenausbeute etwas eingehender betrachten. Schon in der ersten Mitteilung haben wir darüber diskutiert, ob man im Gebiet B die Reaktionsgeschwindigkeit der Dianthracenbildung durch die Gleichung

$$\frac{dD}{dt} = k_1 A A' \quad (1)$$

zum Ausdruck bringen soll, wo A bzw. A' die Konzentration des normalen bzw. angeregten Anthracenmoleküls und D die Zahl der gebildeten Dianthracenmoleküle vertritt. Nun ist der mittlere Zeitintervall, worin ein Quant von der Reaktionslösung absorbiert wird $1/J$, andererseits ist die mittlere Lebensdauer des angeregten Anthracenmoleküls $1/Z_{A'=1}$, wo $Z_{A'=1}$ die Gesamtstosszahl in einer Volumeinheit stattfindet, wodurch ein A' -Molekül entweder in die Dianthracenbildung oder in die Zurückverwandlung ins normale Anthracenmolekül eingeht. Daraus ergibt sich die Zahl $n_{A'}$ der A' -Molekül in cm^3 ,

$$n_{A'} = \frac{J}{V Z_{A'=1}}, \quad (2)$$

wo V das Volum des Reaktionsgefäßes ist. $Z_{A'=1}$ ist wieder proportional der Zahl der Stosspartner des A' -Moleküls d.h. der normalen Anthracenmoleküle und ist zu setzen

$$Z_{A'-1} = n_A Z_{A'-1, A-1}, \quad (3)$$

wo $Z_{A'-1, A-1}$ bloss durch diese Gleichung zu definieren ist.

Die Gesamtzahl des normalen bzw. angeregten Anthracenmoleküle im Gefäss vom Volum V ist $n_A V$ bzw. $n_{A'} V$, und wir können hierbei auch mit recht annehmen, dass $e^{-\frac{E}{RT}}$ - ten Teil der normalen Anthracenmoleküle beim Zusammenstoss mit angeregten in die Reaktion zur Bildung von Dianthracen eingeht. Dann nimmt die Gleichung (1) die folgende Form an

$$\frac{dD}{dt} = k' Z_{A-1, A'-1} n_A V n_{A'} V \exp\left(-\frac{E}{RT}\right), \quad (4)$$

wo k' eine Konstante und E die Aktivierungsenergie dieses elementaren Prozesses sind. R und T haben die übliche Bedeutung. Indem man die Ausdrücke (2) und (3) in (4) einsetzt, bekommen wir

$$\frac{dD}{dt} = k' V J \exp\left(-\frac{E}{RT}\right), \quad (4')$$

und wenn man berücksichtigt, dass $\frac{dD}{dt}$ die Molekülzahl der pro Sek. umgesetzten Anthracenmoleküle ist, wird die Quantenausbeute φ dieser Umsetzung in diesem Gebiet

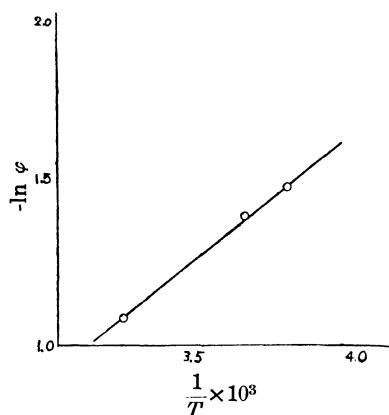


Fig. 3.

Tabelle 3.

Quantenausbeute der Photopolymerisation des Anthracens
in Toluollösung mit einem monochroma-
tischen Licht von $366\mu\mu$.

Versuchstemperatur (°C)	$\frac{1}{T} \times 10^3$	Umgesetzte Menge des Anthracens. D Molekülzahl/Sek.	Quantenausbeute φ	$\ln \varphi$
-10	3.802	5.83 10^{14}	0.219	-1.497
0	3.666	6.63 „	0.249	-1.399
30	3.301	9.01 „	0.338	-1.085

J : Die von der Anthracenlösung absorbierte Lichtquantenzahl von $366\mu\mu$ pro Sek. = 2.66×10^{15}

φ : $\frac{D}{J}$

T : Absolut Temperatur.

$$\varphi = \frac{dD}{dt}/J = k'V \exp\left(-\frac{E}{RT}\right) \quad (5)$$

und

$$\ln \varphi = k - \frac{E}{RT}, \quad (5')$$

wo k wieder eine neue Konstante ist.

Aus dieser Formel kann man den Zahlenwert von E bei den verschiedenen Versuchstemperaturen berechnen, dessen Ergebnisse in Fig. 3 dargestellt wurde, wo $-\ln\varphi$ als Ordinate gegen $\frac{1}{T}$ als Abzisse aufgetragen.

Daraus ersieht man, dass die Kurve geradlinig verläuft und aus ihrer Neigung erhält man die Aktivierungsenergie. Der daraus berechnete Zahlenwert von E beträgt 1.75 Kal./Mol. Durch die Extrapolation der Kurve von Fig. 3 gewinnt man für den Zahlenwert der Quantenausbeute bei der Temperatur von 167° den Wert 0.44, der mit dem von Weigert bekommenen Wert gut übereinstimmt.⁽³⁾

Zusammenfassung.

1. Die Bildungsgeschwindigkeit des Dianthracens aus Anthracen in Toluollösung wurde noch weiter durchstudiert, und zwar bei verschiedener Temperatur sowie bei verschiedener Belichtungszeitdauer.

2. Die Quantenausbeute dieser Umsetzung mit monochromatischem Licht von 366 μ wurde bestimmt und aus der Benutzung des aus den Messungen gewonnenen Temperaturkoeffizienten haben wir den Wert von Weigert extrapoliert. Die beiden Werte erwiesen sich in guter Übereinstimmung.

Die vorliegende Untersuchung wurde durch das Stipendium der Ausgaben des Unterrichtsministeriums für wissenschaftliche Forschung unterstützt. Es ist mir eine angenehme Pflicht, Herrn Prof. Dr. Katayama für die wertvollen Hinweise zu danken. Bei den Messungen hat meine Assistentin Frl. T. Akimoto mitgearbeitet, wofür ich ihr auch hiermit danke.

*Institut für physikalische Chemie der
Toritsu-Hochschule, Tokio.*

(3) Weigert, *Naturwiss.* **15** (1927), 124.

Étude biochimique sur les éléments des terres rares. I. Sur la distribution du néodyme dans les viscères.

Par Réinosuké HARA.

(Reçu le 21 février 1949.)

Introduction. Jusque'ici, les études systématiques sur la biochimie des éléments des terres rares ont été faites au laboratoire pharmacologique de l'université de Wurzburg⁽¹⁾ et de Florence.⁽²⁾ Je pouvais obtenir le néodyme bien pur par la cristallisation fractionnée en employant le nitrate de magnésium, et mettre à profit cette terre rare pour faire les présentes études systématiques. Ces études systématiques du néodyme ont été faites récemment par G. Guidi.⁽³⁾ On a d'abord déterminé sa pureté au moyen de l'analyse spectroscopique à rayons X.

Les conditions de l'expérience sont comme suivante.

Appareil employé—type Siegbahn.

Cristal—Spath.

Courant électrique—5 mA.

Position du cliché—Nd $L\alpha_1$, et Er $L\alpha_1$.

Tension électrique—15 KV.

Temps d'exposition—60 minutes.

Le résultat de l'analyse est montré dans la table 1.

Table 1.

position du cliché ligne	Nd $L\alpha_1$	Er $L\alpha_1$
Nd $L\alpha_1$	##	
Nd $L\alpha_2$	≠	
Nd $L\beta_1$	+	
Nd $L\beta_2$		##
Pr $L\alpha_1$	+	
Pr $L\alpha_2$	+	
Pr $L\beta_1$	±	
Pr $L\gamma_1$		±
La $L\beta_1$	±	
La $L\beta_2$	±	
Sm $L\alpha_1$	+	
Sm $L\beta_1$		±
Sm $L\gamma_1$		±

— très fort ≠ — assez fort
+ — faible ± — très faible

Le néodyme employé contient la petite quantité de Pr, et les quantités minimum de Sm et de La. Cette expérience a été faite pour connaître certains mouvements du néodyme dans l'organisme. Autrefois, comme Guidi a étudié, l'absorption et l'évacuation du néodyme étaient très peu. Quand le néodyme est donné aux animaux par injection intra-

(1) S. Hara, *Arch. f. exper. Path.*, **100** (1923), 217 (Ce); H. Steidle et M. Ding, *Arch. f. exper. Path.*, **141** (1929), 273 (Y); H. Steidle et H. Dürr, *Arch. f. exper. Path.*, **145** (1929), 19 (Sm).

(2) M. Ajazzi-Mancini, *Arch. di. Fisiol.*, **24** (1926), 162; **25** (1927), 43, 257, 373 (La); P. Niccolini et G. Guidi, *Boll. Soc. ital. Biol. sper.*, **4** (1929), 1051 (La, Nd, Pr.); G. Guidi, *Arch. internat. Pharmacodynamie*, **37** (1930), 305; **39** (1930), 1 (Nd); P. Niccolini, *Arch. internat. Pharmacodynamie*, **37** (1930), 199 (Pr); P. Niccolini, *Arch. internat. Pharmacodynamie*, **40** (1931), 247 (Sm); P. Niccolini, *Boll. Soc. ital. Biol. sper.*, **6** (1931), 202, 204; **7** (1932), 998 (Nd. Pr. Sm).

(3) G. Guidi, *Arch. internat. Pharmacodynamie*, **37** (1930), 305; **39** (1931), 1.

veine, intramusculaire, on ne peut jamais trouver cet élément dans l'évacuation. J'ai examiné le mouvement de cet élément dans l'organisme au moyen de l'analyse spectroscopique à rayons X.

Expérience. animal— le rat, au poids du corps de 70–100g.

Conditions de l'expérience. D'après G. Guidi,⁽⁴⁾ en la solution à 1.666% chlorure du néodyme est isotonique contre le sang, et d'après L.C. Maxwell,⁽⁵⁾ le dose mortelle du chlorure du néodyme aux rats est 30–40mg./kg. en injection intraveine. J'ai injecté 0.2c.c. de la solution du chlorure du néodyme à 1.5% une fois par jour pendant deux jours. Cinq jours après, on a dissequé le rat et a confirmé par l'analyse spectroscopique à rayons X. Les conditions de cette analyse sont mêmes que la détermination de la pureté.

Table 2.

		NdL α_1	NdL α_2	NdL β_1	Pr L α_1	Pr L β_1			NdL α_1	NdL α_2	NdL β_1	Pr L α_1	Pr L β_1
foie	1	⦿	+	+	±	±	cœur	1	±				
	2	+	+	+				2	±				
	3	⦿	+	+	±	±		3					
	4	⦿	+	+	±			4	+	±	+		
	5	⦿	+	+	±	±		5	±				
rate	1	+	+	+			poumon	1	⦿	+	+	±	
	2	⦿	+	+	±			2	+	±	+		
	3	⦿	+	⦿	+	±		3	+	±	±		
	4	⦿	+	+				4	+	±	±		
	5	⦿	+	+	±	±		5	+	±	±		
rein	1						estomac, intestin et leurs contenus	1	+	±			
	2	±						2	+	±	+		
	3	±						3	+	±	+		
	4							4	+	±	+		
	5	±						5	+	±	+	±	±
pan- créas	1						"1,2,3,4,5" indiquent les numéros des animaux. ⦿ -- très fort ⦿ -- assez fort + -- faible ± -- très faible						
	2												
	3												
	4	±											
	5												

(4) G. Guidi, *Arch. internat. Pharmacodynamie*, **37** (1930), 306.

(5) L. C. Maxwell et F. Bischoff, *J. Pharmacol.*, **43** (1931), 61.

Les résultats de l'analyse spectroscopique à rayons X sont montrés dans la table 2.

Mêmes après cinq jours d'injection, on peut trouver une très grande quantité de ce sel dans chaque viscère, et sur cinq rats, dans le foie et la rate, la ligne $NdLa_1$ qui est la ligne de la mise évidence est presque toujours forte ou assez forte, et on peut trouver aussi les lignes $NdLa_2$, $NdL\beta_1$, et les lignes $PrLa_1$, $PrL\beta_1$. On peut trouver la ligne $NdLa_1$ et de plus les lignes $NdLa_2$, $NdL\beta_1$ au poumon. On n'a pas trouvé la ligne $NdLa_1$ aux pancréas, rein, et cœur, ou si on l'a trouvée, l'intensité du $NdLa_1$ est négligeable. Dans l'estomac, l'intestin, et leurs contenus, on a trouvé les lignes $NdLa_2$, $NdL\beta_1$ autre de la ligne $NdLa_1$, et pour un seul cas, les lignes $PrLa_1$ et $PrL\beta_1$.

Concentration du néodyme dans l'évacuation. Pour cinq rats, on a décomposé toute évacuation de sept jours dans le flacon Kjeldahl par l'acide sulfurique et par l'acide azotique. On a ensuite ajouté l'acide chlorhydrique pour dissoudre sulfate du calcium. Par l'addition d'hydroxyde du natrium, en obtenant le précipité d'hydroxyde, on l'a fait dissoudre dans l'acide chlorhydrique, et ajouté 5mg. du chlorure du cérium (exempt des Nd, La, Sm). On a alors obtenu le précipité enduit par l'acide oxalique et procédé l'analyse spectroscopique à rayons X après la calcination de ce précipité. Les résultats de l'analyse sont montrés dans la table 3.

Table 3.

Nd La_1	Nd La_2	Nd $L\beta_1$
≡	+	≡

Conclusion. (1) En donnant le sel du néodyme à l'organisme, il change au certain composé insoluble, se dépose dans chaque viscère et son évacuation est très peu remarquable. C'est-à-dire même après cinq jours d'injection, on peut trouver très grande quantité de ce sel au chaque viscère et ne peut trouver dans l'évacuation au moyen de l'analyse spectroscopique à rayons X.

(2) En un mot, les viscères dans lesquels se dépose le sel sont phagocyte, tels le système réticulendothériale et la cellule épithériale du poumon. Sur cinq rats, le sel a été trouvé remarquablement dans le foie et la rate. On peut aussi trouver le sel dans le poumon.

(3) Les viscères où le sel ne se dépose guère sont le pancréas, le rein, et le cœur.

(4) L'analyse spectroscopique à rayons X pour l'évacuation des cinq rats a donné les résultats suivants. La ligne $NdLa_1$ est forte, on a trouvé aussi les lignes $NdLa_2$, $NdL\beta_1$, mais leurs intensités sont plutôt faibles pour sept jours d'évacuation.

À la fin de ce compte-rendu, je devoué mes reconnaissances plus profondes à M. le Prof. Kenjiro Kimura pour les instructions extrêmement soigneuses.

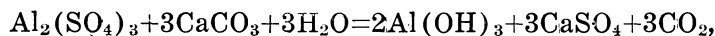
The Reaction of Aluminum Sulfate and Calcium Carbonate. I. Preparation of Basic Aluminum Sulfate Sol and its Hydrolysis

By Tsutomu KUWATA and Tadahisa NAKAZAWA

(Received March 12, 1949.)

Introduction. It has been known that basic aluminum sulfate may be produced by dissolving aluminum hydroxide in aluminum sulfate solution. The solubility of the oxide measured by R. Kremann, K. Hüttinger⁽¹⁾ was relatively small at room temperature and the ratio of Al_2O_3 : SO_3 is about 1 mol:2 mol. N. Grünstein⁽²⁾ has claimed in his patent that pure aluminum hydroxide is prepared by the hydrolysis of basic aluminum sulfate solution containing ferrous sulfate. The solution was produced by reacting iron powder on the concentrated solution of aluminum sulfate containing iron salts. Another patent claimed by G.H. Hultman⁽³⁾ is that the pure basic aluminum sulfate is precipitated by calcium carbonate from the dilute solution of aluminum sulfate and ferrous sulfate.

If we assume that the reaction of calcium carbonate and aluminum sulfate is as follows,



3 mols of CaCO_3 are necessary for 1 mol of $\text{Al}_2(\text{SO}_4)_3$. But the reaction is neither so simple nor so perfect.

Change of the Composition of Aluminum Sulfate Solution with the Amount of Reacting Calcium Carbonate. In this experiment a known amount of calcium carbonate in milky state was added little by little in 100c.c. of aluminum sulfate solution under a vigorous agitation in the course of 4–5 hrs. An unvigorous agitation or a quick addition of calcium carbonate is unfavorable for the reaction, because they often induce the formation of large crystals of calcium carbonate or the covering of the carbonate with small crystals of calcium sulfate.

After the whole amount of calcium carbonate was added, the agitation was continued for 30 minutes, and then the precipitate was filtered. The analysis of the filtrate was carried out in the usual manner: i.e. Al_2O_3 by the gravimetric method and $\text{SO}_4^{''}$ by the volumetric method using benzoic acid hydrochloride as the precipitation agent. The pH of the filtrate was observed by the test paper.

(1) R. Kremann, K. Hüttinger, *Jahresb. Geol. Reichsanst., Wien*, **58**, 637, (1908).

(2) N. Grünstein, *Brit. P.*, 472, 229 (1937).

(3) G. H. Hultman., *U. S. P.* 1,607,279 (1926).

Table 1.
The relation between the amount of the reacted carbonate
and the composition of the filtrate.

No.	CaCO ₃ add. % to equivalent	Al ₂ O ₃ concn		SO ₃ concn.		SO ₃ /Al ₂ O ₃ molar ratio
		g./c.c.	% to original concn.	g./c.c.	% to original concn.	
Solution I	—	0.0856	100	0.2040	100	2.97
1	60.0	0.0879	102.7	0.1021	50.1	1.47
2	75.0	0.0355	41.5	0.0392	19.3	1.33
3	89.9	0	0	0.0035	1.7	—
4	99.9	0	0	0.0018	0.9	—
Solution II	—	0.1178	100	0.2810	100	3.03
1	58.6	0.1221	103.6	0.1613	57.5	1.68
2	76.2	0.1205	102.2	0.1262	44.9	1.33
3	93.9	0.0521	44.2	0.0525	18.7	1.28
4	117.3	0	0	0.0043	1.6	—
Solution III	—	0.1231	100	0.2758	100	2.85
1	59.9	0.1288	104.6	0.1651	60.0	1.63
2	74.5	0.1316	106.9	0.1218	44.3	1.18
3	85.5	0.1274	103.5	0.1103	40.1	1.10
4	99.3	0.0516	41.9	0.0533	19.3	1.31

The Solutions II and III correspond to the saturated solution at
ca. 20° and 38–40°C respectively.

In the above table, some data which overrun from the original concentration of Al₂O₃ would be accounted for the concentration of the solution being taken off some water for the crystallization of calcium sulfate. The results obtained are shown in Fig. 1.

While the concentration of SO₃ decreases linearly in proportion to the amount of the CaCO₃ added, the aluminum content in the solution does not decrease in the same manner and the more concentrated solution can retain more aluminum in the solution. As a result, highly basic aluminum sulfate sol may easily be obtained from the concentrated solution of aluminum sulfate by this process.

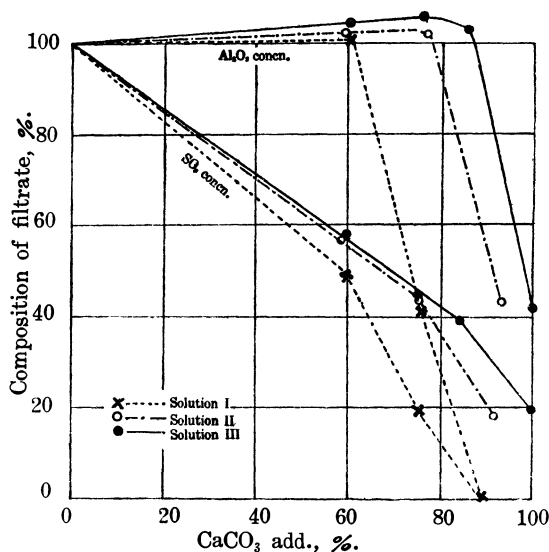


Fig. 1. The relation of the amount of reacted CaCO₃ and the composition of the filtrate.

The reaction of CaCO₃ with the solution of aluminum sulfate, however, is somewhat delicate. If the addition of CaCO₃ is too quick, an insoluble form of basic aluminum sulfate deposits with CaSO₄. In such a

case, the decrease of molar ratio $\text{SO}_3/\text{Al}_2\text{O}_3$ of the solution stops at an unsatisfactory extent. It is also interesting that the small overcharge of calcium carbonate causes the almost perfect precipitation of the insoluble basic aluminum sulfate.

Sol-Gel Transformation. The concentrated and highly basic aluminum sulfate solutions, like solutions II-No. 3 in Table 1, are viscous and transparent with a faint blue fluorescence. They are relatively stable and unvariable for the stock of several months at room temperature, although some samples deposit, in these standings, the white fairly dense precipitates. When the stable and highly basic aluminum sulfate solutions are heated up to 50-70°C, they coagulate to opaque gelatinous gels. Since this sol-gel transformation is reversible according to temperature, it again changes to the original sol form when standing at room temperature. This

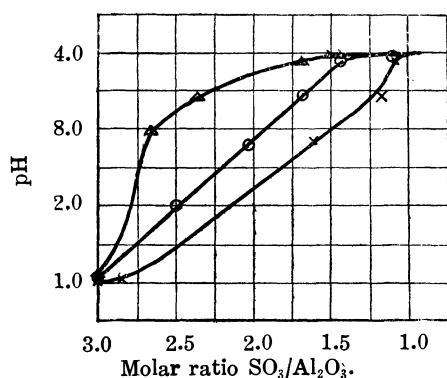


Fig. 2. The relation of pH and $\text{SO}_3/\text{Al}_2\text{O}_3$ of solution.

Δ , $\circ$, $\times$ are the solutions I, II, III in Table 1 respectively.

remarkable phenomena of highly basic aluminum sulfate solution is assumed to be accounted for the change of hydration degree of associated aluminum hydroxysulfate molecules. The details are left for a future study.

pH of the Basic Aluminum Sulfate. The relation of pH and molar ratio $\text{SO}_3/\text{Al}_2\text{O}_3$ of the basic aluminum sulfate solution is not definite. It differs with the concentration of Al_2O_3 . The more dilute solution of basic aluminum sulfate shows the larger value of pH at the same

value of $\text{SO}_3/\text{Al}_2\text{O}_3$, though in all cases, the pH becomes about 4.0 after all.

Hydrolysis of the Basic Aluminum Sulfate. When the basic aluminum sulfate solution is thrown into water, a while precipitate is

Table 2.

The relation between $\text{SO}_3/\text{Al}_2\text{O}_3$ of the solutions and the yields of Al_2O_3 by their hydrolysis.

No.	Composition of solution Al_2O_3 g./c.c.	$\text{SO}_3/\text{Al}_2\text{O}_3$	Yield of the precipitate (observed as Al_2O_3) %
1-1	1.274	1.10	79.8
1-2	"	"	81.4
2	0.502	1.27	64.9
3	0.282	1.44	57.6
4	0.202	1.58	52.9
5	0.125	1.73	52.0

No. 1-2 was thrown into the water at 20°C. and not heated.

readily produced. This precipitate is a kind of basic aluminum sulfate having the molar ratio $\text{Al}_2\text{O}_3:\text{SO}_3=1:0.5-0.6$. It corresponds to the com-

The concentration of solution observed as Al_2O_3 g./c.c.: (1) 0.0501, (2) 0.104 (3) 0.123

position of $2\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot x\text{H}_2\text{O}$. It is fairly dense and can easily be filtered.

Five c.c. of the basic aluminum sulfate are thrown into 50 c.c. of water at 80°C . and well stirred and then filtered. The relation of $\text{SO}_3/\text{Al}_2\text{O}_3$ of the basic aluminum sulfate and the yield of the precipitate are shown in Table 2. and Fig. 3.

It seems that in spite of the distinction of the concentration of the basic aluminum sulfate solution, the yield of Al_2O_3 is in a linear relation with $\text{SO}_3/\text{Al}_2\text{O}_3$ of the basic solution.

The preparative method of aluminum hydroxide or alumina studied by the present authors is also of much interest for the separation of aluminum and iron from their sulfate solution, because ferrous sulfate does not show such hydrolytic change.

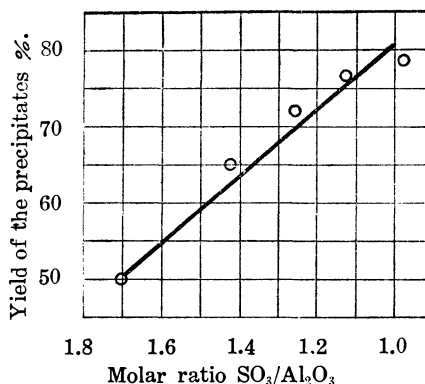


Fig. 3.

Summary

1. By the moderate reaction of calcium carbonate and the concentrated solution of aluminum sulfate, highly basic aluminum sulfate sol is easily obtained.

2. Some kinds of the basic aluminum sulfate sol become gel on heating and the sol-gel transformation is perfectly reversible at the neighbourhood of $40\text{--}50^\circ\text{C}$.

3. On dilution with water, the highly basic aluminum sulfate ($\text{SO}_3/\text{Al}_2\text{O}_3=1.1\text{--}1.6$) hydrolyses and precipitates the insoluble basic aluminum sulfate ($(\text{SO}_3/\text{Al}_2\text{O}_3=0.5\text{--}0.6)$).

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this paper, the former two under the conditions of the diffusion-control have been dealt with, in which, since the oxidation-reduction of simple (or hydrated) metal ions gives the more general formula, the formula for it is derived first and that for the deposition of metal is represented as one in particular conditions. The reduction or the oxidation-reduction of organic compounds is to be reported in the succeeding papers, as well as the electrode reaction of the complex metal ions and, further, the various electrode reactions under the conditions of the non-diffusion-control. As for the dissolution of the dropping mercury electrode the derivation of the formula has been furnished by Eyring⁽²⁾ in the more general case of the dissolution of metals.

Oxidation-reduction of simple (or hydrated) metal ions. Consider the net electrode reaction represented by the equation (1), in which adsorption, decomposition, polymerisation and the like are not assumed to occur at the electrode surface.



where M^{m+} and $M^{(m-n)+}$ symbolize the oxidized and the reduced forms of simple (or hydrated) metal ions respectively. Consider a potential-energy barrier to exist between the initial state, the oxidized form M^{m+} , and the final state, the reduced form $M^{(m-n)+}$. If the free energy difference of the initial and the activated states and that of the final and the activated states are represented by ΔF_1 and ΔF_2 respectively, the difference of ΔF_1 and ΔF_2 becomes the free energy difference of the initial and the final states, which is represented by ΔF_0 .

Assume that the reaction in which the oxidized form is reduced at the electrode surface is the forward reaction and the reaction in which the reduced form is oxidized at the electrode surface is the reverse reaction, and that the potential difference between the electrode and the solution, V , acts completely between the initial and the final states of the electrode reaction. If α is the fraction of the potential V that is operative between the initial and the activated states, the potential αV will facilitate the forward reaction and $(1-\alpha)V$, retard the reverse reaction, and then the rates of the forward and the reverse reactions are represented by the equation (2)

$$\begin{aligned} \text{forward reaction: } & s \cdot \frac{kT}{h} [A_o] e^{-\Delta F_1/RT} e^{-\alpha V F/RT} \equiv [A_o] \kappa_1 E_1 \\ \text{reverse reaction: } & s \cdot \frac{kT}{h} [A_R] e^{-\Delta F_2/RT} e^{(1-\alpha) V F/RT} \equiv [A_R] \kappa_2 E_2, \end{aligned} \quad (2)$$

where s is the constant which depends on the nature of the electrode, $[A_o]$ and $[A_R]$ represent the activities of the oxidized and reduced forms

at the electrode surface respectively, and κ_1, κ_2, E_1 and E_2 are the abbreviations of $s \frac{kT}{h} e^{-\Delta F_1/RT}$, $s \frac{kT}{h} e^{-\Delta F_2/RT}$, $e^{-n\alpha VF/RT}$ and $e^{n(1-\alpha)VF/RT}$ respectively. In the equation (2) it is also considered that in the reaction concerned the forward reaction is facilitated when the electrode potential becomes more negative.

Since the magnitude of current flowing is determined by the difference of the two rates, the current, assumed to be cathodic, is

$$I = n \varepsilon \{ [A_o] \kappa_1 E_1 - [A_R] \kappa_2 E_2 \}. \quad (3)$$

On the other hand, since, in polarography, the current flowing depends almost entirely on the diffusion because of the existence of large excess of indifferent electrolytes, it can be represented by the diffusion equations for the oxidized and the reduced forms, as mentioned below:

$$I = n \varepsilon K_o ([C_o]^\circ - [C_o]) = n \varepsilon K_o / f_o ([A_o]^\circ - [A_o]) = n \varepsilon K_o' ([A_o]^\circ - [A_o]) \quad (4)$$

$$I = n \varepsilon K_R ([C_R] - [C_R]^\circ) = n \varepsilon K_R / f_R ([A_R] - [A_R]^\circ) = n \varepsilon K_R' ([A_R] - [A_R]^\circ) \quad (5)$$

$[C_o], [C_R]$: concentrations of the oxidized and reduced ions at the electrode surface.

$[C_o]^\circ, [C_R]^\circ$: concentrations of the oxidized and reduced ions in the bulk of the solution.

$[A_o]^\circ, [A_R]^\circ$: activities of the oxidized and reduced ions in the bulk of the solution.

f_o, f_R : activity coefficients of the oxidized and reduced ions in the solution.

K_o, K_R : constants concerning the diffusion of the oxidized and reduced ions.

If it is assumed that the electrode reaction and the diffusion are kept in an equilibrium at the electrode surface, I , $[A_o]$ and $[A_R]$ can be written as the function of V , $[A_o]^\circ$ and $[A_R]^\circ$ using the equations (3), (4) and (5). The expression of $[A_o]$ is obtained as the equations (6) and (6') and that of $[A_R]$, as the equations (7) and (7').

$$[A_o] = \frac{K_o' [A_o]^\circ (\kappa_2 E_2 + K_R') + K_R' [A_R]^\circ \kappa_2 E_2}{K_R' \kappa_1 E_1 + K_o' K_R' + K_o' \kappa_2 E_2} \quad (6)$$

$$= \frac{[A_o]^\circ \left(\frac{1}{K_R'} \frac{\kappa_2 E_2}{\kappa_1 E_1} + \frac{1}{\kappa_1 E_1} \right) + \frac{1}{K_o'} [A_R]^\circ \frac{\kappa_2 E_2}{\kappa_1 E_1}}{\frac{1}{K_o'} + \frac{1}{\kappa_1 E_1} + \frac{1}{K_R'} \frac{\kappa_2 E_2}{\kappa_1 E_1}}$$

$$= \frac{[A_o]^\circ \left(\frac{1}{K_R'} + \frac{1}{\kappa_2 E_2} \right) + \frac{1}{K_o'} [A_R]^\circ}{\frac{1}{K_o'} \frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2} + \frac{1}{K_R'}} \quad (6')$$

$$\begin{aligned}
 [A_R] &= \frac{K'_o[A_o]^\circ \kappa_1 E_1 + K'_R[A_R]^\circ (\kappa_1 E_1 + K'_o)}{K'_R \kappa_1 E_1 + K'_o K'_R + K'_o \kappa_2 E_2} \\
 &= \frac{\frac{1}{K'_R} [A_o]^\circ + [A_R]^\circ \left(\frac{1}{K'_o} + \frac{1}{\kappa_1 E_1} \right)}{\frac{1}{K'_o} + \frac{1}{\kappa_1 E_1} + \frac{1}{K'_R} \frac{\kappa_2 E_2}{\kappa_1 E_1}} \quad (7) \\
 &= \frac{\frac{1}{K'_R} [A_o]^\circ \frac{\kappa_1 E_1}{\kappa_2 E_2} + [A_R]^\circ \left(\frac{1}{K'_o} \frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2} \right)}{\frac{1}{K'_o} \frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2} + \frac{1}{K'_R}} \quad (7')
 \end{aligned}$$

Substituting the equations (6) and (7) or (6') and (7') for $[A_o]$ and $[A_R]$ in the equation (3), I is written as follows:

$$\begin{aligned}
 I &= \frac{n \varepsilon K'_o K'_R ([A_o]^\circ \kappa_1 E_1 - [A_R]^\circ \kappa_2 E_2)}{K'_R \kappa_1 E_1 + K'_o K'_R + K'_o \kappa_2 E_2} \\
 &= n \varepsilon \frac{[A_o]^\circ - [A_R]^\circ \frac{\kappa_2 E_2}{\kappa_1 E_1}}{\frac{1}{K'_o} + \frac{1}{\kappa_1 E_1} + \frac{1}{K'_R} \frac{\kappa_2 E_2}{\kappa_1 E_1}} \quad (8)
 \end{aligned}$$

$$\begin{aligned}
 &= n \varepsilon \frac{[A_o]^\circ \frac{\kappa_1 E_1}{\kappa_2 E_2} - [A_R]^\circ}{\frac{1}{K'_o} \frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2} + \frac{1}{K'_R}} \quad (8')
 \end{aligned}$$

Since $\frac{\kappa_2}{\kappa_1} = e^{-\Delta F'_0/RT} = e^{-nV_0 F/RT}$, where V_0 symbolizes the normal oxidation-reduction potential, the following relation is obtained.

$$\frac{\kappa_2 E_2}{\kappa_1 E_1} = e^{n(V - V_0)F/RT}$$

Now, the assumption that the oxidation-reduction reaction concerned is controlled completely by the diffusion will be introduced. When the rate of reduction of the oxidized form at the electrode surface is extremely large compared with the rate of diffusion of the oxidized form, that is, $\frac{1}{\kappa_1 E_1}$ is negligible compared with $\frac{1}{K'_o}$ and when the rate of oxidation of the reduced form at the electrode surface is extremely large compared with the rate of diffusion of the reduced form, that is, $\frac{1}{\kappa_2 E_2}$ is negligible compared with $\frac{1}{K'_R}$, the same equation for current, the

equation (9), can be derived in both cases, but from the equation (8) in the former case and from the equation (8') in the latter case.

$$I = n \varepsilon K'_o K'_R \frac{[A_o]^\circ - [A_R]^\circ e^{n(V-V_0)F/RT}}{K'_R + K'_o e^{n(V-V_0)F/RT}} \quad (9)$$

Further, the equation (10) is obtained by rearranging the equation (9).

$$e^{n(V-V_0)F/RT} = \frac{K'_R}{K'_o} \frac{n \varepsilon K'_o [A_o]^\circ - I}{I + n \varepsilon K'_R [A_R]^\circ} \quad (10)$$

The equations (9) and (10) express the relation of the electrode potential and the current, which are nothing but the formulae of the current-voltage curve in polarography.

The limiting case when the difference of V and V_0 is large should be considered. There are two cases, of which the one occurs when V is much more positive than V_0 , and the other occurs when V is much more negative than V_0 . In the first case $e^{n(V-V_0)F/RT}$, that is, $\frac{\kappa_2 E_2}{\kappa_1 E_1}$ becomes large and then $\frac{\kappa_1 E_1}{\kappa_2 E_2}$ becomes small; in other words $\frac{\kappa_1 E_1}{\kappa_2 E_2}$ is nearer to zero, the larger the difference of V and V_0 . Then, for the equation for the current, the equation (11) is obtained from the equation (8) or (8') using the assumption of the diffusion-control:

$$I = -n \varepsilon K'_R [A_R]^\circ = -n \varepsilon K_R [C_R]^\circ \equiv (I_a)_R. \quad (11)$$

This represents nothing but the diffusion current for the anodic wave. Moreover it proves from the equation (7) or (7') that $[A_R]$ is equal to zero in this condition.

In the second case, on the other hand, $e^{n(V-V_0)F/RT}$, that is, $\frac{\kappa_2 E_2}{\kappa_1 E_1}$ comes nearer to zero and then the equation for current is derived by the same manner as the equation (11).

$$I = n \varepsilon K'_o [A_o]^\circ = n \varepsilon K_o [C_o]^\circ \equiv (I_a)_o. \quad (12)$$

This expresses the diffusion current for the cathodic wave. In this case it proves from the equation (6) or (6') that $[A_o]$ is equal or nearly equal to zero.

From the equations (11), (12) and (10), is obtained

$$e^{n(V-V_0)F/RT} = \frac{K'_R}{K'_o} \frac{(I_a)_o - I}{I - (I_a)_R}, \quad (13)$$

which is the formula of current-voltage curve employed most generally

in polarography.

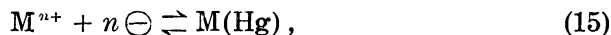
When $\kappa_1 E_1$ and $\kappa_2 E_2$ have a magnitude which is nearly the same and when they are both extremely large compared with K'_o and K'_r , from the equations (6) and (7) or (6') and (7') is obtained

$$\frac{e^{n(V-V_0)F/RT}}{e} = \frac{[A_o]}{[A_r]}. \quad (14)$$

This is the same as the Nernst's equation which expresses the static electrode potential.

Finally the following must be emphasized. In the direct derivation of the formula of the current-voltage curve in polarography that is based on chemical kinetics, two fundamental assumptions are taken: the one is that the electrode reaction at the electrode surface and the diffusion are strictly kept in an equilibrium, and the other is that the rates of all of the possible intermediate steps in the oxidation-reduction reaction are so much more rapid than the diffusion that the current at any point on the polarographic wave is diffusion-controlled. However, to attain the equations (9) and (10), it is not absolutely necessary that both rates of the electrode reactions of the oxidized and the reduced forms are much larger than the rates of diffusions of corresponding forms. In other words, if the rate of diffusion of oxidized form can be rate-determining, it makes no difference whether on the reduced form the rate of electrode reaction is larger than the rate of diffusion or smaller. The converse is also true. This is obvious by the fact that the same equation, the equation (9), can be derived from the equations (8) and (8') in the corresponding cases. To obtain the Nernst's equation, on the other hand, it is absolutely necessary that both rates of the electrode reactions of the oxidized and the reduced forms have the magnitude nearly the same as each other, and they are much larger than the rates of the diffusions of the corresponding forms.

Deposition of metals from simple (or hydrated) metal ions. In this case the following reaction should be considered instead of the equation (1).



where M^{n+} symbolizes the simple (or hydrated) metal ion of n valences and $M(Hg)$, amalgam of the metal deposited by the electrode reaction.

If the activities of the metal ion and the metal in amalgam at the electrode surface are represented by $[M^+]$ and $[M]$ respectively and the activities of the metal ion in body of solution and the metal in body of the dropping mercury electrode, by $[M^+]^\circ$ and $[M]^\circ$, $[M^+]$, $[M]$, $[M^+]^\circ$ and $[M]^\circ$ correspond to $[A_o]$, $[A_r]$, $[A_o]^\circ$ and $[A_r]^\circ$ respectively in the equations (2) to (14) described above. Therefore, the equations for the

deposition of metal can be obtained by substituting $[M^+]$, $[M]$, $[M^+]^\circ$ and $[M]^\circ$ for $[A_o]$, $[A_R]$, $[A_o]^\circ$ and $[A_R]^\circ$ respectively in those equations. In this case K'_R signifies a constant concerning the diffusion of the metal in mercury.

If the case when pure mercury is employed for the dropping mercury electrode is taken up, the activity of the metal in body of the dropping mercury electrode, $[M]^\circ$, can be regarded as zero, and hence $[A_R]^\circ$ can be substituted by zero. As the result of this substitution, the following equations are obtained for the formula of the current-voltage curve in polarography, corresponding to the equations (9) and (10).

$$I = \frac{n \varepsilon K'_o K'_R [M^+]^\circ}{K'_R + K'_o e^{n(V-V_o)F/RT}} \quad (16)$$

$$e^{n(V-V_o)F/RT} = \frac{K'_R}{K'_o} \frac{n \varepsilon K'_o [M^+]^\circ - I}{I} \quad (17)$$

As to the equation for diffusion current, in the case of the oxidation-reduction reaction two equations are obtained; the one, for cathodic, and the other for anodic. In this case, however, for the diffusion current only one equation, the equation (18), is given, since $(I_d)_R$, that is, the equation (11) becomes zero because $[M]^\circ$ which corresponds to $[A_R]^\circ$ in the equation (11) is zero.

$$I = n \varepsilon K'_o [M^+]^\circ \equiv I_d. \quad (18)$$

Summary.

The formula of the current-voltage curve in polarography has been derived from the view-point of chemical kinetics and independently of the Nernst's equation. As a result, it has been clearly shown that if the condition of the diffusion-control is fulfilled the formula which had been derived from the Nernst's equation has been obtained in the various types of the electrode reaction. Of these types both the oxidation-reduction of the simple (or hydrated) metal ions and the deposition of the metals from the simple (or hydrated) metal ions have been dealt with in the present paper.

It is also suggested that the "irreversible wave" which cannot be treated theoretically based on the Nernst's equation can possibly be dealt with by the similar derivation as mentioned here.

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Étude biochimique sur les éléments des terres rares. II. Sur l'absorption du néodyme dans le corps animal.

Par Réinosouké HARA

(Reçu le 21 février, 1949)

Introduction. Jusqu'ici, par l'administration *pérorale*, l'absorption du sel des terres rares a été faite par C. Bachaem,⁽¹⁾ G. Baehr et H. Wessler,⁽²⁾ R. Niccolini,⁽³⁾ et l'injection intramusculaire par G. Baehr. et Wessler,⁽⁴⁾ M. Ajazzi-Manchini,⁽⁵⁾ P. Niccolini,⁽⁶⁾ G. Guidi.⁽⁷⁾ Ils ont démontré que l'absorption des sels du néodyme dans le corps animal est très peu considérable. Je l'ai étudiée par l'analyse spectroscopique à rayons X. Les sels employés sont le chlorure du néodyme soluble, et l'oxalate du néodyme insoluble.

Expérience

Dans le cas de l'administration pérorale. En employant trois rats, j'ai donné à chaque animal 0.05 g de chlorure du néodyme ou d'oxalate du néodyme par jour, pendant cinq jours. Après cela, ces rats ont été tués et on a incinéré les viscères et procédé à l'analyse spectroscopique à rayons X. Le résultat de l'analyse est montré ci-dessous.

(a) *Dans le cas de chlorure du néodyme.*

Table 1.

		NdL α_1	NdL α_2	NdL β_1	PrL α_1	PrL β_1		NdL α_1	NdL α_2	NdL β_1	PrL α_1	PrL β_1
foie	1	##	+	+	±	±	pancréas	1	++	±	±	
	2	++	+	+				2	+	±		
	3	++	+	+	±			3	+			
rate	1	++	+	+	±		poumon	1	++	±	+	±
	2	++	+	+				2	+	±		
	3	##	+	+	±	±		3	+	±		
rein	1	++	±	+			coeur	1	+			
	2	+	±					2	+	±		
	3	+						3	+	±		

— très fort, ++ — assez fort, + — faible, ± — très faible

"1, 2, 3," indiquent les numéros des animaux.

(1) C. Baechaem, *Arch. internat. Pharmacodynamie*, **17** (1907), 381.

(2) G. Baehr et H. Wessler, *Arch. internat. Med.*, **2** (1908), 517.

(3) P. Niccolini, *Arch. internat. Pharmacodynamie*, **37** (1930), 222; **40** (1931), 262.

(4) G. Baehr et H. Wessler, *Arch. internat. Med.*, **2** (1908), 526.

(5) M. Ajazzi-Manchini, *Arch. di. Fisiol.*, **25** (1927), 43.

(6) P. Niccolini, *Arch. internat. Pharmacodynamie.*, **37** (1930), 221; **40** (1931), 261.

(7) G. Guidi, *Arch. interuat. Pharmacodynamie.*, **37** (1930), 344; **39** (1930), 1.

(b) Dans le cas de l'oxalate du néodyme.

Table 2.

		Nd L α_1		Nd L α_1			Nd L α_1	
foie	1	±	rein	1		poumon	1	±
	2	±		2	±		2	±
	3			3			3	±
rate	1		pancréas	1		coeur	1	±
	2	±		2			2	±
	3	±		3	±		3	

Par l'administration *pérorale* du sel soluble, dans le foie et la rate, la ligne Nd L α_1 est très forte ou assez forte à peu près sans exception, et on a trouvé en outre les lignes Nd L γ_2 , Nd L γ_3 , Pr L α_1 , Pr L γ_2 . Aux autres viscères, on a trouvé les lignes Nd L α_1 , Nd L γ_2 . C'est peut-être que le sel a changé en forme insoluble dans le sang, et s'est fixé dans chaque viscère. Par l'administration *pérorale* du sel insoluble, on a trouvé la ligne Nd L α_1 très faible dans chaque viscère.

Dans le cas de l'injection intramusculaire. En employant trois rats, j'ai fait l'injection intramusculaire 0.4 c.c. de la solution du chlorure du néodyme à 0.5% à chaque animal, au

Table 3.

		NdL α_1	NdL α_2	NdL β_1	PrL α_1	Pr L β_1			NdL α_1	NdL α_2	NdL β_1	Pr L α_1	PrL α_1
foie	1	++	±	+			poumon	1	+	+			
	2	++	±	+				2	++	±	+		
	3	++	+					3	+	+			
rate	1	+++	+	+	±	±	coeur	1	+	+	+		
	2	++	±	+	±			2	++	±		±	
	3	++	±	+	±			3	+	+			
pancréas	1	+					estomac, intestin et leurs contenus	1	+				
	2	+						2					
	3	+	+					3					
rein	1	+	±				endroit de l'injection	1	+++	+	+	±	±
	2	+						2	+++	+	+	±	±
	3	+	±					3	+++	+	+	±	±

(8) G. Guidi, *Arch. internat. Pharmacodynamie.*, **37** (1930), 318.

dos. Cinq jours après, je les a tués et incinéré les viscères, et fait l'analyse spectroscopique à rayons X. D'après G. Guidi,⁽⁸⁾ le dose mortelle du chlorure du néodyme aux rats est 0.15-0.25 g./kg.

Le resultat de l'analyse est montré dans la table 3.

Dans le cas d'injection intramusculaire, la ligne Nd L_{x1} dans l'endroit de l'injection est très forte sans exception, et on a trouvé les lignes Nd L_{x2} , Nd $L_{\beta1}$, Pr L_{x1} , Pr $L_{\beta1}$.

Conclusion, (1) Par l'administration *pérorale*, l'absorption du sel soluble (chlorure du néodyme) n'est pas remarquable. Et de même l'injection intraveine, le sel a été trouvé dans le foie et la rate. Aux autres viscères, on a trouvé le sel, c'est peut-être que le sel a changé en forme insoluble dans le sang, et s'est fixé dans chaque viscère.

(2) Par l'administration *pérorale*, le sel insoluble (oxalate du néodyme) est absorbé en petite quantité, c'est-à-dire, on a trouvé la ligne N_{α} , très faible dans chancs chaque viscère.

(3) En l'injection intramusculaire, l'absorption du chlorure du néodyme est très faible, la plus grande quantité est fixée dans l'endroit de l'injection. De même dans les autres cas, dans le foie et la rate, on a trouvé le sel. Dans les autres viscères, on a trouvé le sel sans exception car le sel est fixé dans le sang.

(4) Quand on donne au corps animal les sels du néodyme par diverses méthodes, l'absorption et l'évacuation sont très faibles car les sels changent à certaine forme insoluble dans l'organisme, et se déposent dans les viscères constitués en grande partie par le système réticulendothériale.

À la fin de ce compte-rendu, je dévoue mes reconnaissances plus profondes à M. le Prof. Kénjiro Kimura pour les instructions extrêmement soigneuses, à M. le Prof. Kéigi Misawa et à M. le Prof. adjoint Taro Kawamura pour les conseils favorables au sujet des expériences zoologiques et à M. M. les Profs. Taku Uémura, Eiji Ochiai, et Yosoji Ito et à M. le Prof. adjoint Kazuo Kuroda pour les suggestions pleines de pénétrations.

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Fungus and Enzyme.

Preparation of *Aspergillus Oryzae* Amylase

By Taichi HARADA.

(Received March 1, 1949).

The role of fungi in nature is of very great importance to our daily life.

Pathogenic fungi are those which cause a very annoying disease "Eczema" in the human body⁽¹⁾ and also plant diseases in plants. Non-pathogenic species are those which cause deterioration and destruction of timbers, textiles and foods, and those which produce many organic acids,⁽²⁾ e. g. citric, lactic, gluconic, kojic, etc., arsine compounds, penicillin,⁽³⁾ etc. and also those which produce many important enzymes, e. g. amylase, protease, tannase, invertase, etc. This is, of course, speaking in a broad sense of the difference between the pathogenic and the non-pathogenic species.

The amount of the enzymes produced by fungi depends upon the composition of culture medium in which they are grown. According to Takada⁽⁴⁾ wheat bran increases the production of *Asp. oryzae* enzyme as much as two times as that of embryo of rice bud and five times as that of oil removed bean. In this connection the author refers to his previous paper⁽⁵⁾ in which very important precautions of making Koji were pointed out.

In the preservation of enzyme in the Koji cake the cake may be dried to prevent bacterial infections or after crushing the cake loosely the enzyme may be extracted at once with cold water and then filtered and preserved in a manner suitable for the purpose for which the preparation is to be used. Sodium chloride at the saturation point gives the most satisfactory results as an antiseptic. This solution may be used for most purposes; oral administration, food preparation or for the desizing of textiles. The amylase prepared from the water extract by alcohol precipitation is not a pure single enzyme but a mixture of many enzymes.⁽⁶⁾

(1) T. Harada, *This Bulletin*, **9** (1934), 186, 192.

(2) Prescott and Dunn, "Industrial Microbiology", McGraw-Hill Book Co., New York (1940).

(3) Fleming, *Brit. J. Exp. Path.*, **10** (1929), 266; "Penicillin", Hekiso Soc., Kawade Book Store, Tokyo (1946); also Sumiki's "Penicillin", Sangyo Tosho Co., Tokyo (1946).

(4) *J. Brew. Assn. Japan*, **22** (1944), 232; also Takada, Katsui and others, *J. Appl. Micology*, **2** (1948), 88.

(5) T. Harada, *Ind. Eng. Chem.*, **23** (1931), 1424.

(6) Inouye, "Useful Molds", Hokko Book Store, Tokyo (1948).

(7) T. Harada, *Ind. Eng. Chem. Anal. Ed.*, **3** (1931).

In the factory, in precipitating the enzyme with alcohol we often encounter great trouble when the Koji water extract becomes unusual in nature giving a colloidal (light) or a gummy (heavy) precipitate which can not be thoroughly dehydrated. In other words, it does not give a flocculent precipitate. When a gummy precipitate is obtained, it must be dissolved in water and then the precipitation must be carried out again. Such a colloidal or a gum-like precipitate could not be easily dried or if it is dried a dark lump may be obtained. In both cases not only is it very difficult to make it in powder form after drying, but the diastatic strength becomes greatly lost. Of course the trouble of gummy formation may be removed by cutting down the amount of alcohol but this decreases the enzyme. It was found that, in case the precipitate tends to become colloidal, an addition of a small amount of sodium phosphate, or potassium phosphate, or the like to the extract not only solves the trouble but also gives an increase of diastatic power to the preparation in its total strength. However, in the case of gummy formation the dibasic halogen compound will solve the trouble but it will decrease the total Lintner's value (L. V.). This is due to a destruction of the enzyme.

Experimental

Influence of Inorganic Salts upon Amylase Precipitation. Twenty five cubic centimeters of the water extract of Koji were mixed with a small amount of inorganic salts to which 75 c.c. of alcohol were added for the precipitation. It was mixed well, filtered, dried and finally the strength determined by the author's⁽⁷⁾ method for L.V.

Table 1.

Salts (0.05 g.)	Yield (g.)	Tested L.V.	Total L.V.
$(\text{NH}_4)_2\text{SO}_4$	0.6370	3816	2431
KH_2PO_4	0.6211	4133	2567
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.6377	4133	2636
K_2HPO_4	0.6475	3933	2547
$\text{Na}_2\text{HPO}_4 \cdot 5\text{H}_2\text{O}$	0.6595	4033	2660
Alcohol alone	0.6361	3617	2301

Original total L.V. of 25 c.c. of the extract $(111 \times 25) = 2775$

Table 2.

Salts	(g.)	Yield (g.)	Tested L.V.	Total L.V.
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.05	0.6330	2875	1820
"	0.10	0.6635	2450	1626
"	0.20	0.6910	1500	1037
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.05	0.5710	3075	1756
"	0.10	0.6480	1825	1183
"	0.20	0.7680	1000	768
Alcohol alone		0.6190	3075	1903

Original total L.V. of 25 c.c. of the extract $(159 \times 25) = 3975$

Table 3.

Salts (0.10 g.)	Yield (g.)	Tested L.V.	Total L.V.
NaCl	0.6714	4775	3206
NaHCO ₃	0.8250	3975	3280
Na(NH ₄) ₂ PO ₄ ·4H ₂ O	0.6925	4450	3082
MgSO ₄ ·7H ₂ O	0.7580	4175	3165
(NH ₄) ₂ HPO ₄	0.6817	3773	2573
K ₂ HPO ₄	0.6965	4175	2908
Alcohol alone	0.6905	3975	2745
Original total L.V. of 25 c.c. of the extract (159 × 25) = 3975			

Table 4.

Salts (g.)	Yield (g.)	Tested L.V.	Total L.V.
MgCl ₂ ·6H ₂ O 0.10	0.6765	5725	3873
" 0.20	0.7145	3975	2840
CaCl ₂ ·2H ₂ O 0.10	0.6625	5100	3379
" 0.20	0.8045	1525	1227
Alcohol alone	0.6560	6350	4166
Original total L.V. of 25 c.c. of the extract (191 × 25) = 4775			

Preparation of Dry Amylase without Alcohol for Oral Purpose. In preparing the amylase in tablet form for oral administration, the Koji extract was mixed with magnesium or calcium carbonate in the ratio of about three to one and placed in a large flat container and while slowly mixing it, it was dried by means of a dry air current at low temperature (30–35°C). L.V. of the mixture was obtained up to 750. This amylase-carbonate mixture may be easily made into tablets.

Summary

1. The influence of inorganic salts upon the precipitation of amylase with alcohol under given conditions has been studied.
2. The preparation of dry amylase without alcohol for oral purpose has been described.

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Studies on Foams. III. The Foam Formation of Some Dyestuff Solutions.

By Masayuki NAKAGAKI.

(Received March 14, 1949)

It has been reported, in the preceding paper⁽¹⁾, that the abilities of foam formation of some mixtures of organic liquids are correlated with the volume contraction on admixture, and the latter may probably be related with the amphipathy of solute molecules. That is to say, the balance between the polar and non-polar portion of the molecule has been considered as an essential factor governing the foam formation. If this might be true also of dyestuff solutions known as "micelle colloids", some connection may be found among the foam formation, surface activity, and molecular structure of the dyestuffs.

The foam formation and the surface tension have been measured on the aqueous solutions of congo red and five triphenyl methane dyes: methyl violet 5 B, brilliant green, malachite green (crystallized), crystal violet (chemical pure), and Hofmann's violet. E. Merck's dyes have been used without further purification, excepting congo red, which has been purified by the sodium acetate-alcohol method. Dyestuff solutions were preserved for 1 to 36 weeks as the solution of 1g./l., and diluted just before the measurements.

The foam formation was measured by the shaking test; 20 c.c. of the solution was taken into a test tube, 40 c.c. in capacity, and 1.8cm. in diameter and provided with a glass stopper. This was shaken up and down for 30 seconds at the rate of 3 times a second and at the amplitude of 25 cm. The maximum foam zone height A_m (cm.) is considered as a measure of the foaminess of the solution. The foam strength τ (sec./cm.) is defined as the reciprocal of the collapsing velocity of foam within the initial thirty seconds. Thus,

$$\begin{array}{ll} \tau = 30/(A_m - A_{30}) & \text{for } t > 30, \\ \text{or } \tau = t/A_m & \text{for } t < 30, \end{array}$$

where A_{30} is the foam height after 30 seconds from the instant of maximum foam height, and t is the foam duration in seconds. The foaming ability (F') of the solution (Fig. 1) is defined as the products of foaminess (A_m) and foam strength (τ). The surface tension was measured by du Nouy's tensiometer. The viscosities of these solutions were also measured, and concluded that they have no appreciable effects on the foam formation, since the values relative to water are 1.00 to 1.02.

(1) The second paper, This Bulletin, 22 (1949), 21.

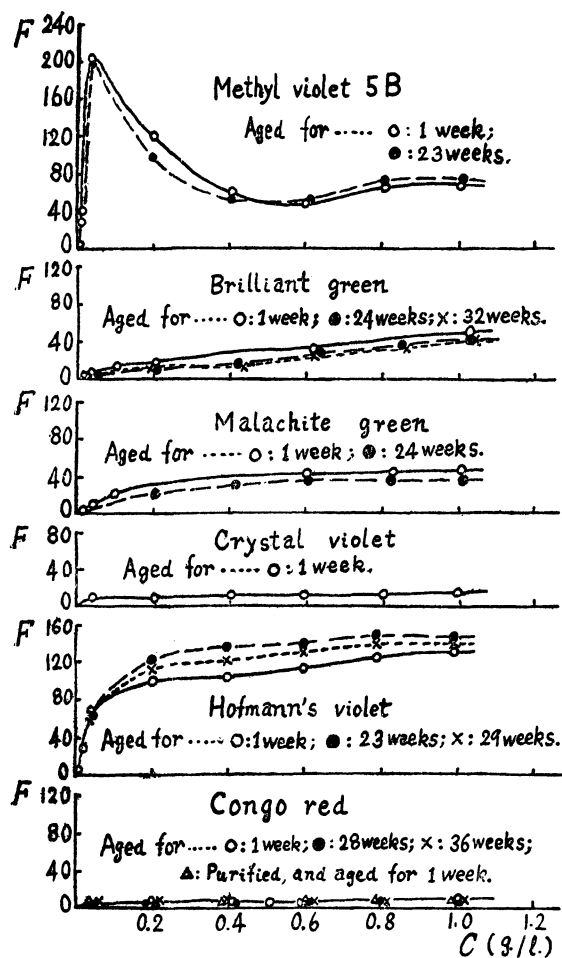


Fig. 1. Foaming Abilities.

Calvin.⁽⁴⁾ On the other hand, malachite green or brilliant green has a phenyl radical which lacks the amino group, and this part of the molecule shows distinct hydrophobic character. Then, the molecule having both polar and non-polar parts in the molecule was named by G. S. Hartley⁽⁵⁾ as "amphipathic" molecule. Such a molecule is adsorbed to the surface of the solution, turning the polar part to water and the non-polar part to air, and lowers the surface tension and increases the foam formation; the degree of which is greater when the hydrophobic character of the non-polar part is more distinct or the hydrophilic character

The effect of aging of the solution on the foam formation is not serious, and the change of foam formation by the purification of dye is also insignificant.

It is shown in Table 1 that the solution of large foaming ability has small surface tension excepting Hofmann's violet. Such a relation may be interpreted as follows. The ion of crystal violet, e. g., undergoes quantum mechanical resonance among three equivalent structures, and in consequence, the molecule takes the shape of a regular triangle, and three nitrogen atoms equally have 1/3 of the positive charge as the average. This was stated by E. Hückel⁽²⁾ and G. N. Lewis and M. Calvin⁽³⁾, and the symmetrical structure interpreted satisfactorily the absorption spectra obtained by G.E.K. Branch and M.

(2) E. Hückel, *Z. Elektrochem.*, **43** (1937), 827.

(3) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25** (1939), 273.

(4) G.E.K. Branch and M. Calvin, "The Theory of Organic Chemistry," pp. 179, New York (1941).

(5) G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts", Chapter 7, Paris (1936).

Table 1. Properties of Dyestuff Solutions. (Aged for one week).

Dyestuff	Concentration		Specific surface tension	Foaming ability	Foaminess	Foam strength	Foam duration
	(g./l.)	(mol/l.)					
			r/r_w	F	A_m (cm.)	τ (sec./cm.)	t (sec.)
Methyl violet 5B	1.01	0.00209	0.86	71	5.1	14	>200
Brilliant green	1.03	0.00214	0.90	47	3.7	12.7	>200
Malachite green	0.827	0.00227	0.94	42	3.1	13.5	42
Crystal violet	0.796	0.00196	0.96	11	8.9	2.8	11
Hofmann's violet	0.988	0.00235	0.96	187	4.7	27	>200
Congo red	1.52	0.00218	0.99	3.4	1.4	2.5	3.4

of the polar part is weaker. This is a qualitative generalization of Traube's rule, which has been applied to homologous series of alcohols and fatty acids by O. Bartsch⁽⁶⁾ and T. Sasaki⁽⁷⁾, but no one attempted hitherto to apply this idea to more complex substances. From this standpoint, however, it is thought to be reasonable that the surface activity and foaming ability of crystal violet, having positive charges on every apex of the regular triangular molecule, are smaller than that of brilliant green or malachite green, having no charge on one of the apexes. Then, comparing the amino group of brilliant green and malachite green, the former is ethylated and the latter is methylated, so that the hydrophilic nature of the former is weaker than the latter. It is, therefore, reasonable that the surface activity and the foaming ability of the former is greater than that of the latter. As to methyl violet 5B, the surface activity and foaming ability are very large, and the foaming ability becomes maximum at a relatively low concentration (Fig. 1), since one of the amino groups is connected with a very large hydrophobic group. One exception is Hofmann's violet, whose surface activity is small while the foaming ability is large. This is thought to be due to the strong interaction between amino groups which are only partially ethylated.

The sequence of the foaming ability of triphenyl methane dye solutions is thus interpreted with their structural formulae. Since the dominant factor is the properties of the molecule itself, it is supposed that the single molecule is mainly concerned with the foam formation and micelle plays no significant role.

Summary

The foam formations of the aqueous solutions of methyl violet 5B, brilliant green, malachite green, crystal violet, Hofmann's violet and congo red have been measured. The foaming ability, that is the product of foaminess and foam strength, is considered as the measure of the

(6) O. Bartsch, *Kolloid-Z.*, **38** (1926), 177.

(7) T. Sasaki, *This Bulletin*, **13** (1938), 517.

foam formation. This scarcely changes by the long period's storage of the solution. The foaming ability of them is nearly parallel with the surface activity. This is interpreted with structural formulae of dye-stuffs.

The author wishes to express his hearty thanks to Professor Jitsusaburo Sameshima for his kind encouragement.

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On the Equilibrium of the Radioactive Elements in the Hydrosphere. VI.⁽¹⁾ Radioactivity Measurement of Natural Waters with the Geiger-Müller Counter:

By Kazuo KURODA.

(Received March, 14, 1949.)

The radioactivity of a large number of natural waters in Japan has been mainly measured with the fontactoscopes, such as Schmidt-type, I.M.-type etc. The radioactivity measurement of natural waters with the Geiger-Müller counter was recently tried for the first time by the present author, and the results are reported in this paper.

Experimental Part. (1) Apparatus. A Geiger-Müller counter of Nippon-Denki Co. was used. The thickness of aluminum wall of the counter tube was about 0.1 mm. and the background was about 30 per minute. (2) Radioactivity measurement. The water sample (about 100 c.c.) was placed near the counter-tube (about 2 cm. from the wall of the counter-tube), and the number of counts per minute was recorded.

Results. (1) Relation between the number of counts and the radon content of natural waters. The results of radioactivity measurement of the radioactive springs of Misasa, Tottori Prefecture are shown in Table 1.

Table 1. Relation between the number of counts and the radon content of mineral water of Misasa.

Name	Radon Content (10^{-10} Curie/Litre)	Number of Counts (Counts/Minute)
Yamada-ku, Kyodo-yu, Nomi-yu	1044	19.5
OTR (Ohasi, Tennen-buro-Reisen)	263	19

(1) Previous Paper V. Kazuo Karoda, This Bulletin, 22 (1949), 149.

Okayama-University	59.5	5
Hanaya	741	8.5
Moto-Aburaya	142.5	3
Eirakuan		3.5
Akasakiya	85	0
Matsubara	111.1	7
Yakuba-no-yu	424	5.5
Gunze-no-yu	1021	15.5
Tap water		5.5
Distilled water	0	2

The number of counts is almost proportional to the radon content of natural water, but the natural waters containing thorium emanation show exceptionally large values of counts, as in the case of spring OTR of Misasa. The sensitivity of radioactivity measurement with the counter was considerably low compared with that of the fontactoscopes. Thus the radioactivity of the springs containing less than 10 Mache-unit of radon could not be detected with the counter.

(2) Increase of β and γ radioactivity of fresh mineral waters. It was reported in the previous paper,⁽²⁾ that the intensity of β and γ radioactivity of fresh mineral water is usually very low, and it increases after the mineral water has issued, and a constant value is obtained within about three hours. It was explained in the previous paper to be due to the increase of the decay products of radon after the mineral waters have issued. This phenomenon was also observed in the case of the radioactivity measurement with the Geiger-Müller counter. The results are shown in Table 2.

Table 2. Increase of β and γ Radioactivity of Fresh Mineral Waters.

Name of the Springs	Time elapsed after the Springs issued (Minutes)	Number of Counts per Minute
Yamada-ku, Kyodo-yu Nomi-yu	15	2.5
	33	4
	63	15.5
	160	20
Yamada-ku, Kyodo-yu (Stagnant Water)	25	12
	73	17
	275	16
Seito-kan, Nomi-yu	22	9
	64	7
	165	17
	238	13
Gunze-no-yu	22	1
	60	15
	117	15
	180	14

(2) Kazuo Kuroda and Yuji Yokoyama, This Bulletin, **21** (1948), 52.

(3) Measurement of radioactivity due to radium with the Geiger-Müller counter. The radioactivity of mineral waters containing radium was measured with the Geiger-Müller counter, several months or several years after the sample was taken. The radioactivity of mineral waters containing high amounts of radium ($n \times 10^{-12}$ to $n \times 10^{-10}$ g. radium per litre) could not be detected with the Geiger-Müller counter, and it was concluded that it is impossible to estimate the radium content of natural waters directly with the counter.

(4) Radioactivity of Sinter Deposits. The radioactivity of sinter deposits of the thermal springs of Misasa and the mineral springs of Masutomi was measured with the Geiger-Müller counter. Some sinter deposits of Misasa showed considerably strong radioactivity, which is almost equal to that of monazite. This radioactivity is considered to be due to radium and mesothorium in the sinter deposits.

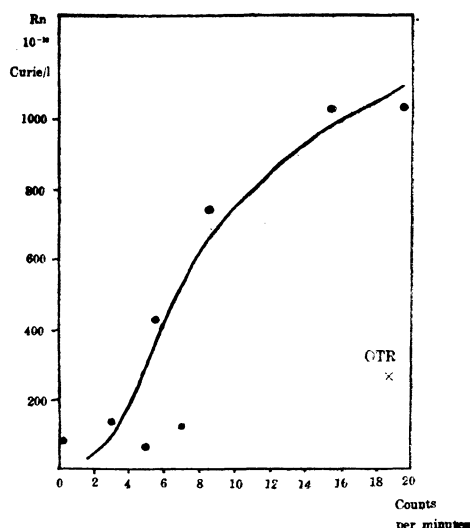


Table 1. Relation between the number of counts and the radon content of mineral waters of Misasa.

Summary

The radioactivity of the natural water was measured with the Geiger-Müller counter. The relationship between the radon content of the thermal springs of Misasa and the number of counts was studied. The increase of β and γ radioactivity of fresh mineral waters was observed.

The author expresses his hearty thanks to Professor Kenjiro Kimura for his kind guidance. The cost of this research was defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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New Method of Determination of Thallium with Cobalt Hexammine Trichloride.

By Yukio MURAKAMI.

(Received March, 31, 1949.)

Introduction. Thallium is usually found in small quantities in association with large amounts of alkali metals and other elements and also contained in chamber muds in plants commercializing sulfuric acid, and in the flue-dust formed during the calcination of iron pyrites, lead ores and zinc blend.

In 1863, W. Crookes proposed the iodide method⁽¹⁾. However, several defects were pointed out by some workers,⁽²⁾ and as a substitute for the iodide method the chromate method was recommended by Moser and Brunkle⁽³⁾ as being most accurate in the determination of thallium. This chromate method had been in general use for a long time, but as the preliminary separation of many metals that are commonly present with thallium is troublesome, besides having to allow a little over 12 hours for complete precipitation, several other methods were in continuous study by many workers. No one proposed method yet has been approved for wide use. On the other hand, the application of the organic reagents, such as thionalide,⁽⁴⁾ mercapto-benzothiazol⁽⁵⁾ and thiourea⁽⁶⁾, to the determination of thallium has been recommended because of their good sensitivity. However, when not more than 10 mg. in a 50 gr. sample of flue-dust and chamber muds containing a large quantity of common metals is to be determined, none of the so-far suggested methods is qualified as a sufficient answer to the problem.

Among the above mentioned methods, the thionalide method is the most sensitive, though it does not show specific reaction to the thallium (Mehrdeutigkeit) and a rough estimation as to the test sample is required before the thionalate formation can be made. In a case of minute

(1) W. Crookes, *Chem. News*, **7** (1863), 133; *J. Chem. Soc.*, **17** (1864), 115; G. Werther, *Z. anal. Chem.*, **3** (1864), 1; H. Baubigny, *Compt. rend.*, **113** (1891), 544; W. Lepper, *Z. anal. Chem.*, **79** (1930), 323.

(2) F. Mach and W. Lepper, *Z. anal. Chem.*, **68** (1926) 40; F. Cuta, *Collection Czechoslovak. Chemical Communications*, **7** (1935), 33; W. Lepper, *Z. anal. Chem.*, **79** (1930), 323, H. Baubigny, *Chem. News*, **64** (1891), 239.

(3) L. Moser and A. Brunkle, *Monatsh.*, **47** (1926), 709; J. Bondanar and A. Terenyi, *Z. anal. Chem.*, **69** (1926), 32; A. Cernotzky, *Z. anal. Chem.*, **93** (1933), 349.

(4) R. Berg and Fahrenkamp, *Z. anal. Chem.*, **109** (1937) 305; R. Berg and W. Roebling, *Angew. Chem.*, **48** (1935), 430.

(5) G. Spacu and K. Kuras, *Z. anal. Chem.*, **109** (1936), 90.

(6) C. Mahr and O. Ohle, *Z. anal. Chem.*, **115** (1939), 256.

thallium determination in such samples as in flue-dust and chamber muds occurring with an abundance of many other metals, it is very difficult and impractical according to the author's experience. The thiourea method with which perchloric acid is required has its defects, due to the formation of an elastic compound resembling india-rubber when confronted with specially large quantities of copper, zinc and lead. Moreover the Tl-thiourea complex has a perceptible solubility even in ice cold water. It is an unsatisfactory method for determination of such minute amounts of thallium as was attempted by the author.

In the face of these difficulties the author has taken interest in a suggestive report by Spacu *et al*⁽⁷⁾ stating that thallium can be determined as $\text{Co}(\text{NH}_3)_6(\text{TlCl}_6)$ which is practically insoluble in a slightly acidic medium. In this paper, though the result of the gravimetric determination of considerable amounts of thallium (80 to 100 mg.) only in a pure salt solution is reported, the experimental conditions are not given in details and examination of the interference of many metals, which is of the most practical importance, was not performed. However it is easy to suppose that the determination of a minute quantity of thallium in such samples with accurate results is possible as the factor for thallium in $\text{Co}(\text{NH}_3)_6(\text{TlCl}_6)$ is the least (0.35346) of all factors in the gravimetric method.

This investigation is based upon the above report and was undertaken for the following purposes: (a) To determine the interference of other metals, if any. (b) To note the experimental conditions and to determine as little as 5 to 10 mg. of thallium. (c) To determine whether it is applicable to the determination of thallium in flue-dust and chamber muds.

Experimental.

(a) **Reagent used.** *Thallium standard solution.* Thallium sulfate, Merck reagent (For Analysis), was recrystallized twice and heated to about 400°C in an electric furnace. The standard solution was prepared by dissolving the salt thus obtained.

Cobalt hexammine trichloride $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ (for the sake of convenience, called luteo salt hereafter). Luteo salt is easily prepared from cobalt chloride, ammonium chloride, silver nitrate and ammonia according to Biltz,⁽⁸⁾ and recrystallized from saturated solution by the addition of hydrochloric acid. The saturated solution, the concentration of which is about 20 M at room temperature, was used. It is desirable that any contaminable matter be filtered off before using and to preserve it in amber colored bottle as decomposition will take place with exposure to light.

(b) **Addition of ammonium chloride.** The original report stated the greater possibility of success by making a precipitation under 2.5N hydrochloric acid solution. The suitable acid concentration in this case was tested as shown in Table 1.

These results indicated that it may be safer to use a 2.5N acid solution as previously reported. However, the lower results were obtained due to incomplete pre-

(7) G. Spacu and A. Pope *Z. anal. Chem.*, **120** (1940), 322.

(8) H. Biltz, „Übungsbeispiele aus der unorg. Experimentalchemie“, S. 165, Leipzig (1913).

Table 1. Acid Concentration

Acid Concentration	Co(NH ₃) ₆ TlCl ₆ (g.)	Tl-found (g.)	Tl-present (g.)	Difference (g.)	Remarks
0.33N HCl	0.0284	0.01004	0.01002	+0.00032	added some NH ₄ Cl
0.66N HCl	0.0288	0.01018	0.01002	+0.00016	instantly pptd.
1.32N HCl	0.0283	0.01000	0.01002	-0.00002	„
1.98N HCl	0.0288	0.01018	0.01002	+0.00016	„
3.30N HCl	0.0298	0.01060	0.01002	+0.00058	luteo salt pptd.
0.82N HNO ₃	0.0265	0.00937	0.00970	-0.00033	„
2.26N HNO ₃	0.0290	0.01025	0.00970	+0.00055	„
3.86N HNO ₃	0.0064	0.00227	0.00970	-0.00743	precipitate dissolved
5.46N HNO ₃	0.0005	0.00047	0.00970	-0.00923	„
1.02N H ₂ SO ₄	—	—	0.00970	-0.00970	not precipitated
2.46N H ₂ SO ₄	0.0237	0.00837	0.00970	-0.00133	„
4.26N H ₂ SO ₄	0.0163	0.00594	0.00970	-0.00376	„
7.86N H ₂ SO ₄	—	—	0.00970	-0.00970	„

ipitation as sometimes happen especially with sulfuric acid or nitric acid solution owing to the amount of chloride ion present being insufficient to form TlCl₆'''. But this difficulty is easily removed by the addition of ammonium chloride as shown in Table 2 and the range of acid concentration is safely extended to about 3N. Moreover the determination can be made in any kind of acid medium.

It was also found that the addition of about 0.5 g. ammonium chloride is responsible for the perfect change of thallium ion into TlCl₆'''. Furthermore it makes possible the determination of thallium as slight as 5mg. gravimetrically indeterminate by any other method up to date. Thallium is not easily oxidized with nitric acid alone, but its complete oxidation can be effected in the presence of any chloride ion. As there is a tendency that hydrolysis of thallic nitrate or sulfate will occur, especially when hot, the formation of TlCl₆''' is sometimes difficult. But ammonium chloride removes also these difficulties. Consequently the addition of ammonium chloride newly recommended is remarkably useful in this instance, especially with sulfuric acid solution most commonly used.

Table 2. Effectiveness of the Addition of NH₄Cl

Acid Concentration	HCl (ml.)	NH ₄ Cl (g.)	Tl-complex (g.)	Tl-found (g.)	Tl-present (g.)	Difference (g.)
2.0N H ₂ SO ₄	15	0.5	0.0324	0.01145	0.01149	-0.00004
2.0N H ₂ SO ₄	15	none	0.0311	0.01099	0.01149	-0.00050
2.0N H ₂ SO ₄	none	0.5	0.0325	0.01149	0.01149	-0.00000
2.0N H ₂ SO ₄	none	none	0.0229	0.00081	0.01149	-0.01068
1.9N HNO ₃	15	0.5	0.0326	0.01152	0.01149	+0.00003
1.9N HNO ₃	15	none	0.0235	0.01007	0.01149	-0.00142
1.9N HNO ₃	none	0.5	0.0308	0.01089	0.01149	-0.00060
1.9N HNO ₃	none	none	0.0237	0.00105	0.01149	-0.01044
2.5N H ₃ PO ₄	none	0.5	0.0301	0.01064	0.01032	+0.00032
2.5N H ₂ SO ₄	5	0.5	0.0304	0.01075	0.01032	+0.00043
2.5N H ₂ SO ₄	5	none	0.0232	0.00997	0.01032	-0.00035

(c) **General procedure.** Oxidation can be easily carried out with some particles of potassium chlorate and about 0.5 g. ammonium chloride added to the boiling solution. Boiling is continued until the volume is reduced to one half, and then it is allowed to stand at room temperature. Thus the solution is ready for the precipitation. If luteo salt solution is added, a brown orange precipitate forms instantaneously. When the temperature

of the solution exceeds 50°C, thallic oxide may be precipitated, the formation of which should be avoided.

Twice the amount of luteo salt solution should be added, though theoretically it is sufficient to add 1.3 times the amount of thallium expected in the solution. The precipitate is decanted with 2% HCl solution and transferred to a glass filter G4. Washing must be continued until the washing solution becomes colorless, usually requiring more than 200 ml. for 10 mg. thallium. The precipitate then is washed three times with 5 ml. each of 95% alcohol followed by three times with ether. The precipitate is then dried at 105°C from a half to an hour, and transferred in desicator to cool at room temperature. Thallium now is weighed as $\text{Co}(\text{NH}_3)_6(\text{TlCl}_6)$ ($F = 0.35346$).

The result agrees with the true value within the errors allowed as shown in Table 3. However deviation may be caused, maximum deviation of results was found less than 1.5% of thallium. The remarkable characteristics of this method is that a minute amount of thallium can be determined with fairly good results by the addition of ammonium chloride without any hazardous operation.

Table 3. Accuracy

Tl-present (g.)	$\text{Co}(\text{NH}_3)_6(\text{TlCl}_6)$ (g.)	Tl-found (g.)	Difference (g.)	Err r %
0.00574	0.0163	0.00576	+0.00002	+0.35
0.00484	0.0135	0.00480	-0.00004	-0.82
0.00968	0.0275	0.00972	+0.00004	+0.41
0.00968	0.0270	0.00954	-0.00014	-1.4
0.00968	0.0269	0.00950	-0.00018	-1.8
0.01148	0.0321	0.01149	+0.00001	+0.00
0.01937	0.0551	0.01949	+0.00010	+0.51
0.01937	0.0543	0.01919	-0.00018	-0.92
0.01937	0.0546	0.01930	-0.00007	-0.35
0.01937	0.0547	0.01940	+0.00003	+0.16
0.02903	0.0822	0.02905	+0.00002	+0.07
0.03980	0.1126	0.03973	-0.00007	-0.18

Proposed Method. For practical application, it is necessary to get sufficient knowledge on the behavior of various other ions on luteo salt. However as this proposed method isolates some ions precipitating with luteo salt, for the sake of convenience, this new method will be discussed before the interference is discussed.

(a) *Proposed Method.* Finely ground sample such as flue-dust and chamber muds is perfectly decomposed by treating with an acid mixture, consisting of one part of water, two parts of HCl and HNO_3 , respectively, and four parts of sulfuric acid, being mixed in the named order. Complete evaporation is important for complete isolation of lead, silica, bismuth and others. Then the cooled residue is disintegrated with 1N hot H_2SO_4 , to which a few drops of H_2O_2 is added to reduce any Tl^{+++} that may have been formed. After a while it is filtered to separate the insoluble matter. Complete extracting with the sulfuric acid is necessary for success. To neutralize the greater part of the free acid, the extracted solution is treated with concentrated sodium hydroxide solution. At this stage a precipitate is formed, which diss-

solves slightly on stirring. The remainder of the free acid is accurately neutralized with sodium carbonate solution. The end point is easily perceived by the slow evolving of carbon dioxide gas.

The solution is then heated to boiling and sulfur dioxide is passed until it cools to room temperature. The precipitate, if present, is filtered off. In this condition, thallium exists as thalious ion. Through the procedure until this stage, lead, bismuth, tin, antimony, and mercury etc. have already been removed. Then the solution is acidified to 1N acid concentration with hydrochloric acid and heated to expel any traces of sulfur dioxide. The solution is now ready for oxidation and precipitation in the same way as has been given in the general procedure, including the washing and weighing.

(b) *Interference.* Interferences by several common ions were tested with proposed method, but no serious interference has been noted under the conditions recommended above. The results have a tendency to be slightly higher than the true value as shown in Table 4. The chief sources of error arise from incomplete neutralization and incomplete treatment with sulfur dioxide or from insufficient washing neglecting to remove any contaminable matter. For example, the luteo salt reacts with cadmium to form an orange-colored complex compound. For best results, twice the amount of washing solution already mentioned as required for washing is necessary. However no fatal dissolution of the thallium complex compound was perceptible due to profuse washing. It is evident from table 4 that minute amounts of thallium as small as 10 mg. or even less can be determined in the presence of many other ions a thousand times greater in quantity.

Discussion. The iodide or chromate method was widely used among the many methods. However, the former tends to give slightly lower results than the real value and requires about 18 hours for the complete precipitation owing to its colloid forming tendency. The latter has an advantage over the former in some respects, but it requires also at least 12 hours for standing and is fatally defective in that thallium chromate formed is by nature perceptibly soluble. Moreover the factor is larger than double that of the proposed method. Thus it is easily conceivable that the determination of such minute amounts of thallium less than 50mg. per 100 ml.⁽⁹⁾ is impossible. But in this respect, the proposed method was found to be definitely satisfactory as shown in Table 4, even in the case of a minute amount as 5 mg. per 100 ml.

Mach *et al.*⁽¹⁰⁾ had found that the determination of thallium in small

(9) J. Bondanar and A. Tereniyi, *Z. anal. Chem.*, **69** (1926), 32.

(10) F. Mach and W. Lepper, *Z. anal. Chem.*, **69** (1926), 42; R.J. Meyer, *Z. anorg. allgem. Chem.*, **24** (1900), 364.

amounts impossible with the above method, can be undertaken as Tl_2O_3 . But even the use of this method in flue-dust is definitely unsatisfactory due to the analogous reasons as mentioned above with the chromate method.

Five most widely used methods involving these methods were discussed by Strecker *et al*⁽¹¹⁾ who concluded that $Tl(I)$ - $Co(III)$ -nitrite is most satisfactory. But the minimum amount determined was 0.1 g. Tl and

Table 4. Determination in the Presence of Other Metals

Ion	Salt used (Amount in g.)	$Co(NH_3)_6(TlCl_6)$ (g.)	Tl -found (g.)	Tl -present (g.)	Diff. (g.)	Precipitate
K ⁺	KCl (10)	0.0326	0.01152	0.01149	+0.00003	
Na ⁺	NaCl (10)	0.0324	0.01145	0.01149	-0.00004	
K Al ⁺⁺⁺	Alum (10)	0.0282	0.00997	0.01000	-0.00003	
SiO ₃ ''	Na ₂ SiO ₃ (5)	0.0300	0.01060	0.01032	+0.00028	filtered
		0.0290	0.01025	0.01032	-0.00007	"
Ca ⁺⁺	CaCl ₂ (5)	0.0287	0.01014	0.01003	+0.00011	
Ti ⁺⁺⁺	Ti(SO ₄) ₂	0.0284	0.01004	0.01003	+0.00001	"
Cr ⁺⁺⁺	CrCl ₃ (5)	0.0284	0.01004	0.01003	+0.00001	
Mn ⁺⁺	MnSO ₄ (5)	0.0301	0.01064	0.01032	+0.00032	
		0.0291	0.01029	0.01032	-0.00003	
Fe ⁺⁺⁺	FeCl ₃ (10)	0.0304	0.01071	0.01032	+0.00039	
		0.0326	0.01152	0.01149	+0.00003	
Co ⁺⁺	CoSO ₄ (5)	0.0296	0.01046	0.01032	+0.00014	
Co ⁺⁺	CoCl ₂ (5)	0.0236	0.01011	0.01003	+0.00008	
Ni ⁺⁺	NiCl ₂ ·6H ₂ O (5)	0.0289	0.01022	0.01003	+0.00019	
		0.0299	0.01053	0.01032	+0.00020	
Cu ⁺⁺	CuSO ₄ ·5H ₂ O (10)	0.0283	0.01000	0.01000	0.00000	
Zn ⁺⁺	Zn(C ₂ H ₃ O ₂) ₂ (5)	0.0284	0.01034	0.01032	+0.00002	
		0.0330	0.01166	0.01149	+0.00017	
AsO ₃ '''	As ₂ O ₃ (5)	0.0287	0.01014	0.01003	+0.00011	
MoO ₄ ''	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O (5)	0.0284	0.01004	0.01003	+0.00001	"
Ag ⁺	AgNO ₃ (10)	0.0281	0.00993	0.01000	-0.00007	"
Co ⁺⁺	Cd(NO ₃) ₂ (10)	0.0284	0.01004	0.01003	+0.00001	
Sn ⁺⁺	SnCl ₂ ·2H ₂ O (5)	0.0283	0.01000	0.01000	0.00000	"
		0.0261	0.00923	0.00986	-0.00063	"
Sb ⁺⁺⁺	SbCl ₃ (5)	0.0279	0.00986	0.01000	-0.00014	"
Ba ⁺⁺	BaCl ₂ ·2H ₂ O (10)	0.0259	0.00916	0.00986	-0.00070	"
		0.0290	0.01024	0.01000	+0.00024	"
Hg ⁺	Hg ₂ (NO ₃) ₂ (5)	0.0289	0.01022	0.01000	+0.00022	"
Pb ⁺⁺	Pb(NO ₃) ₂ (10)	0.0234	0.01004	0.01000	+0.00004	"
Bi ⁺⁺⁺	BiCl ₃ (5)	0.0283	0.01000	0.01000	0.00000	"
Mg ⁺⁺	Mg(NO ₃) ₂ ·6H ₂ O (5)	0.0283	0.01000	0.01000	0.00000	
Zn ⁺⁺	ZnSO ₄ (5)	0.0329	0.01163	0.01149	+0.00014	
Zn ⁺⁺	Zn(C ₂ H ₃ O ₂) ₂ (5)	0.0320	0.01141	0.01132	+0.00009	
NO ₃ '	HNO ₃	0.0326	0.01152	0.01149	+0.00003	
SO ₄ ''	H ₂ SO ₄	0.0324	0.01145	0.01149	-0.00004	
PO ₄ '''	H ₃ PO ₄	0.0286	0.01011	0.01000	+0.00011	
PO ₄ '''	(NH ₄) ₂ HPO ₄	0.0301	0.01064	0.01032	+0.00032	

* Precipitate formed when treated with sulfur dioxide.

(11) W. Strecker and P. de la Pena, *Z. anal. Chem.*, **67** (1926), 257.

the factor exceedingly large (0.6469). Owing to this reason and for the necessity of preliminary separation, it is also unsatisfactory for application to flue-dust. The thionalide method, recommended in the determination of such a little amount as 5 mg., cannot be used in the presence of many metals frequently occurring in flue-dust. Matsubara and Kuwabara⁽¹²⁾ found that the thionalide method and chromate method can only give an approximate quantitative result in such a sample because of the presence of many metals. From such standpoints it may be concluded that the proposed method is remarkably superior to the above mentioned and can be easily applied for the determination of minute amounts of thallium.

The superiority will be summarized in the following:

(a) The addition of ammonium chloride realizes the determination of 5 mg. thallium in any mineral acid medium with fairly good results.

(b) The proposed method is time-sparing, usually only requiring two or three hours from the time the sample is brought into solution. It simplified the procedure for the determination particularly in such a substance as flue-dust which is usually in association with numerous other metals. The veracity of this concluded superiority can be proved by comparing it with the thionalide method having the least factor among many of the other methods already mentioned.

(c) It does not require a troublesome separation, thus eliminating another possible source of error which results from the minute amount of thallium being absorbed on voluminous and absorptive precipitates of iron, manganese etc. as is frequently the case noted in other methods.

(d) The factor is the smallest among any other gravimetric method, thus making possible the determination of a minute amount of thallium present in the sample such as flue-dust which is impossible with any other method.

The author wishes to express his sincere gratitude to Prof. Kenjiro Kimura for advising him to undertake this study and for many valuable suggestions. The author also expresses his thanks to Miss F. Ueda who has taken great interest in this experiment and has rendered invaluable help.

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(12) S. Matsubara and T. Kuwabara, *J. Min. Soc. Japan*, **61** (1945), 7.

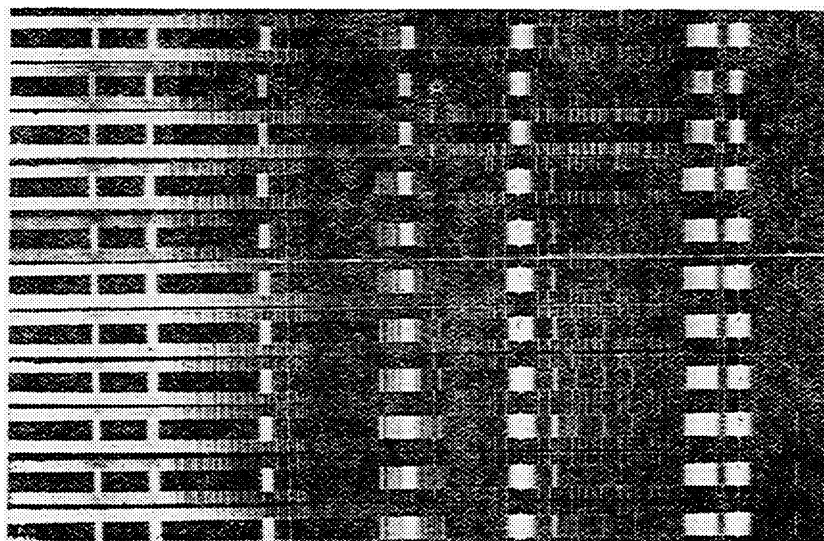
Analysis of Straight-Run Gasolines by Means of the Raman Effect.

By San-ichiro MIZUSHIMA, Shizuo NAKAMURA, and Tsuneo TOBIYAMA.

(Received May 24, 1949.)

The analysis of hydrocarbon mixtures such as gasolines is by no means easy, so far as we adopt only the ordinary chemical procedure. This difficulty can, however, be overcome by the application of Raman effect, because each hydrocarbon molecule has its characteristic Raman lines whose frequencies are not appreciably modified by the presence of other hydrocarbon molecules. The present note deals with the analysis of some straight-run gasolines (end point 150°C) of Sumatra and Borneo by this optical method.

Each of the five samples of straight-run gasolines (Sanga-Sanga, Rantau, Pentopo, Seria, and Miri) were distilled carefully through a long column into 20 ~ 25 fractions and for each fraction the Raman spectrum was measured (see the photograph). Two spectrographs of our own construction were used in this measurement, the larger one having three prisms of the height of 10 ~ 15 cm. From the determination of the in-



The Raman Spectra of Rantau-gasoline (for the fractions of $\sim 30^{\circ}\text{C}$, $30\sim 55^{\circ}\text{C}$, $55\sim 60^{\circ}\text{C}$, $60\sim 65^{\circ}\text{C}$, $65\sim 70^{\circ}\text{C}$, $70\sim 75^{\circ}\text{C}$, $75\sim 80^{\circ}\text{C}$, $80\sim 85^{\circ}$, $85\sim 90^{\circ}\text{C}$, $90\sim 95^{\circ}\text{C}$ and $95\sim 100^{\circ}\text{C}$)

tensity of Raman lines assigned to a definite hydrocarbon⁽¹⁾ these samples were analysed as shown in the table. The components thus determined

Table

Component	Gasoline	Sanga Sanga	Rantau	Pentopo	Seria*	Miri*
Isobutane			T†	T	0.1	0.1
<i>n</i> -butane			T	1	0.1	0.1
2, 2-Dimethyl propane			T	T	T	T
Isopentane		2	1	1	0.5	0.5
<i>n</i> -Pentane		2	1	1	1	1
2, 2-Dimethyl butane		1	1	T	0.2	0.5
Cyclopentane		1	1	1	0.5	1
2, 3-Dimethyl butane		1	2	1	0.3	0.5
2-Methyl pentane }		4	2	4	2.5	2.5
3-Methyl pentane }						
<i>n</i> -Hexane		3	2	5	2.5	1.5
Methyl cyclopentane		2	2	3	1	1.5
2, 2-Dimethyl pentane		1	1	T	0.5	0.1
Benzene		7	1	2	1.8	1.5
Cyclohexane		6	5	3	5	8
2, 4-Dimethyl pentane		2	1	1	0.4	0.1
2, 2, 3-Trimethyl butane			T	T	T	0.05
3, 3-Dimethyl pentane		1	1	T	0.3	0.1
2, 3-Dimethyl pentane			1	1	0.2	0.1
2-Methyl hexane		1	3	3	1.5	1
3-Methyl hexane				3	1	1
3-Ethyl pentane				T	0.1	0.1
<i>n</i> -Heptane		2		9	4	5
2, 2, 4-Trimethyl pentane					T	T
Methyl cyclohexane		11	10	7	14	17
1, 2-Dimethyl cyclopentane		2	2	1	0.1	1.5
Toluene		14	6	7	6	5.5
2, 2, 3-Trimethyl pentane					T	T
2, 3, 4-Trimethyl pentane					T	T
1, 1-Dimethyl cyclohexane					0.5	1
1, 3-Dimethyl cyclohexane		4	4	2	3.5	7
1, 4-Dimethyl cyclohexane		2	4	2	2.5	5
1, 2-Dimethyl cyclohexane			3	2	1.5	5
<i>n</i> -Octane		3		3	3	2
Ethyl benzene		1	1	1	2	1
<i>p</i> -Xylene		2	2	2	2	2
<i>m</i> -Xylene		6	7	5	6	5
<i>o</i> -Xylene		1	4	2	1.5	2
<i>n</i> -Nonane					2	0.5

† T means "trace"

* Seria and Miri gasolines were analysed more carefully than the other three.

(1) As to new data of the Raman spectra of pure *n*-hydrocarbons see Mizushima and Simanouti: J. Am. Chem. Soc. **71** (1949), 1320.

amount to 70 ~ 80 per cent of the original gasolines. The remaining 30 ~ 20 per cent corresponds to the hydrocarbons whose Raman spectra have not been reported.

We thank Miss H. Shirakawa and Mr. M. Morikawa for their assistance in this measurement.

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On the Molecular Association in Amides as Revealed by Their Near-Infrared Absorption Spectra.

By Masamichi TSUBOI.

(Received May 25, 1949.)

As a part of his investigations on the hydrogen bondings in compounds with the peptide linkage, the present writer made some observations of near-infrared absorption spectra of *N*-methylacetamide and δ -valerolactam, two representatives of compounds with the said linkage, one being of the single chain type and the other of the cyclic type. Some of the results obtained are of interest in relation to the general problems of association in amides. It is the purpose of this paper to give the results of the writer's observations of the above-mentioned two substances, and to present a view as to their molecular configurations, and then to discuss some problems of association in amides.

Experimental.

The infrared absorption in the $2.6\sim 3.6\ \mu$ region were measured of *N*-methylacetamide ($\text{CH}_3\text{CONHCH}_3$) and δ -valerolactam ($\begin{smallmatrix} \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\ | & & | \\ \text{CH}_2 & \text{CO} & \text{NH} \end{smallmatrix}$) in liquid state and in carbon tetrachloride solutions.

The optical system of the spectrometer used in the investigation consists of concave mirrors and 60° quartz prism. This was used in conjunction with the thermocouple and galvanometer system. As the source of radiation a tungsten filament lamp in a quartz bulb, running at 80 volts and 1.6 amperes, was used. To determine the wave-lengths of the absorption bands the following standards were used: $2.769\ \mu$ band of phenol, $3.233\ \mu$ and $3.295\ \mu$ bands of benzene, and $3.416\ \mu$ and $3.508\ \mu$ bands of cyclohexane, in dilute carbon tetrachloride solutions.

The samples of *N*-methylacetamide and δ -valerolactam for this investigation were prepared respectively by K. Mayumi and I. Okano and by K. Hoshino and S. Yumoto, to whom the writer's thanks are due. These were subjected several times to vacuum distil-

lation. The melting points determined with the distilled samples were: 28°C for *N*-methylacetamide and 40°C for δ -valerolactam. Carbon tetrachloride used as the solvent, which was washed with water, dried over phosphorus pentoxide, and distilled, was confirmed to give no absorption band due to impurities in the said region of the spectra.

Results and Their Interpretations.

In Tables 1 and 2 certain results obtained by the present measurements are shown. (Cf. Figs. 1 and 2.)

Table 1. Infrared absorptions in 3 μ region of *N*-methylacetamide.

States	Temperatures (°C)	Wave-lengths (in μ) of absorption maxima, with molar absorption coefficients in parentheses		
		Free <i>N-H</i> band	<i>N-H</i> association bands	
In CCl ₄ solution				
Concentrations { 0.0014 mol/l.	15	2.88 (17)		
0.0032	15	2.88 (14)	2.97 (9)	
0.031	13	2.88 (12)	3.00 (33)	3.22 (18)
„	40	2.88 (14)	2.97 (15)	
0.079	16	2.88 (9)	3.03 (35)	3.22 (27)
„	39	3.88 (9)	2.99 (25)	3.22 (12)
Liquid state	30		3.03 (73)	3.22 (54)

Table 2. Infrared absorptions in 3 μ region of δ -valerolactam.

States	Temperatures (°C)	Wave-lengths (in μ) of absorption maxima, with molar absorption coefficients in parentheses		
		Free <i>N-H</i> band	<i>N-H</i> association bands	
In CCl ₄ solution				
Concentrations { 0.0015 mol/l.	15	2.92 (11)	3.11 (41)	3.24 (26)
„	50	2.92 (16)	3.11 (18)	3.24 (10)
0.016	13	2.92 (6)	3.11 (46)	3.24 (38)
„	50	2.92 (12)	3.11 (18)	3.24 (12)
0.023	13	2.92 (4)	3.11 (49)	3.24 (40)
„	40	2.92 (7)	3.11 (28)	3.24 (23)
Liquid state	40		3.09 (55)	3.23 (30)

As is seen from the tables, the absorption intensity for the band at 2.88 μ of *N*-methylacetamide in carbon tetrachloride solution increases with lowering of the concentration of the solution and with rise of its temperatures; while the reverse was observed as to the absorption intensities for the bands at 2.97 ~ 3.03 μ and 3.22 μ . This fact may be explained, as usual, by assigning the band at 2.88 μ to the N-H vibration of the free molecules and the bands at 2.97 ~ 3.03 μ and 3.22 μ to the N-H vibrations of the associated molecules. In the same way, the absorption at 2.92 μ of δ -valerolactam may be assigned to the N-H vibration in the free molecules of δ -valerolactam, and the bands at 3.11 μ and 3.24 μ to the N-H vibrations in its associated molecules. It is thus shown

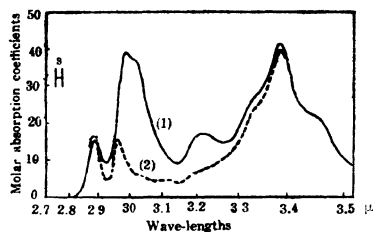


Fig. 1. Absorption curves of *N*-methylacetamide in CCl_4 solution (0.031 mol/l), (1) at 13°C , (2) at 40°C . (s: Slit width)

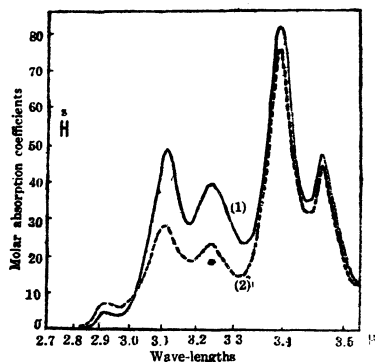


Fig. 2. Absorption curves of δ -valerolactam in CCl_4 solution (0.023 mol/l), (1) at 13°C , (2) at 40°C (s: Slit width)

that the molecules of *N*-methylacetamide as well as those of δ -valerolactam associate through their intermolecular $\text{N-H}\cdots\text{O}$ bondings. There are, however, remarkable differences, as enumerated below, between these two kinds of molecules in the absorption intensities and the positions of the bands in their 3μ region absorption spectra, indicating the difference in their modes of molecular association.

(i) The N-H band (at 2.92μ) of the free molecule of δ -valerolactam is located at a longer wave-length than that (at 2.88μ) of the free molecule of *N*-methylacetamide. This shows that the N-H bonding in the δ -valerolactam molecule is perturbed a little to weaken the bonding, in comparison with that in the *N*-methylacetamide molecule, even in the monomer state—i. e. intramolecular perturbation.

(ii) The tendency of molecular association in carbon tetrachloride solutions is stronger for δ -valerolactam than for *N*-methylacetamide. Thus, even at such a low concentration as 0.0015 mol/l., δ -valerolactam molecules are for a major part in associated state, while at about the same concentration (0.0014 mol/l.), *N*-methylacetamide molecules are in isolated state. In other words, the change in free energy (ΔF) accompanying the dissociation of dimer is much greater for δ -valerolactam than for *N*-methylacetamide.

(iii) With lowering of concentration of the solution or with rise of its temperature, there takes place the shift of the absorption maxima of the N-H association band of *N*-methylacetamide, from 3.03μ to 2.97μ , but no such shift of the absorption maxima of the bands of δ -valerolactam. This fact indicates that there can be only one kind of associated molecules of δ -valerolactam, while there are more than one kind of associated molecules of *N*-methylacetamide, in the respective solutions.

The molecular configurations of *N*-methylacetamide and δ -valerolac-

tam that are consistent with what have been stated above are as follows:

N-Methylacetamide. In the molecule of *N*-methylacetamide, the hydrogen on the nitrogen is *trans*⁽¹⁾ to the oxygen: $\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{H} \text{---} \text{N} \text{---} \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{CH}_3 \end{array} \end{array}$. The associated molecules, which cause the $2.97 \sim 3.03 \mu$ bands, are chain type polymers: $\cdots \text{H} \text{---} \text{N} \begin{array}{l} \nearrow \text{C} = \text{O} \end{array} \cdots \text{H} \text{---} \text{N} \begin{array}{l} \nearrow \text{C} = \text{O} \end{array} \cdots$ or $\cdots \text{H} \text{---} \text{N} \begin{array}{l} \nearrow \text{C} = \text{O} \end{array} \cdots \text{H} \text{---} \text{N} \begin{array}{l} \nearrow \text{C} = \text{O} \end{array} \cdots$,

the adjacent molecules being combined through the single $\text{N} \text{---} \text{H} \cdots \text{O}$ bonding. On this configuration, polymers of various lengths are possible, in consistence with the indication that there are more than one kind of associated molecules of *N*-methylacetamide.

δ -Valerolactam. In the molecule of δ -valerolactam, the hydrogen on the nitrogen is *cis* to the oxygen: $\begin{array}{c} \text{H} \\ | \\ \text{N} \text{---} \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \end{array} \end{array}$. The intramolecular perturbation, mentioned in (i), may be attributed to the attraction between these hydrogen and oxygen atoms, viz. the intramolecular hydrogen bonding: $\text{N} \text{---} \text{H} \cdots \text{O}$. The associated molecules, which cause the 3.11μ band, are ring dimers: $\begin{array}{c} \text{O} \cdots \text{H} \text{---} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{N} \text{---} \text{H} \cdots \text{O} \end{array}$, the two molecules being combined through the double $\text{N} \text{---} \text{H} \cdots \text{O}$ bondings. This configuration is consistent with the indication that there is only one kind of associated molecules of δ -valerolactam. Further, intermolecular double bondings in δ -valerolactam, in contrast to the single bonding in *N*-methylacetamide, account for the greater dissociation energy in the latter.

A few words may be added here concerning the 3.22μ association band of *N*-methylacetamide. In its pure liquid state, this band is comparable in absorption intensity with the 3.03μ band. It is not apparent to the writer, to what this 3.22μ band is to be assigned. But, since the Raman spectra⁽²⁾ in the region of the skeletal frequencies of the *N*-methylacetamide molecule show that in its pure liquid state only one skeletal structure is possible, and moreover since the writer's observation reveals that the molecule of *N*-methylacetamide, is *trans*, this 3.22μ band must be due to something in the associated molecules consisting

(1) In a molecule with the ---CONH--- linkage, the $\text{C} \text{---} \text{N}$ bond has some double-bond character, due to resonance, $\text{O}=\text{C} \text{---} \text{NH} \text{---} \leftrightarrow \text{O}^{\ominus} \text{---} \text{C}=\text{NH}^{\oplus} \text{---}$; and this tends to cause the molecule to take the coplaner configuration, i.e. *trans* $\begin{array}{c} \text{O} \\ || \\ \text{C} \text{---} \text{N} \\ | \quad | \end{array}$ or *cis* $\begin{array}{c} \text{O} \\ || \\ \text{C} \text{---} \text{N} \\ | \quad | \end{array}$ configuration.

(2) S. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka. (To be published.)

only of *trans* molecules. Buswell and others⁽³⁾ assigned the 3.22μ band of monosubstituted amides to the ring dimer structure of their associated molecules, componental monomer of which must be of *cis* form. In the light of what has been just mentioned, this view is not appropriate for the 3.22μ band of *N*-methylacetamide. More information than we have at present is needed before we can discuss further this question. A fact, perhaps worthy of mention in the present connection, is that neither the Raman line for this band nor the infrared absorption band corresponding to its overtone has ever been observed.⁽²⁾

As to the assignment of the 3.24μ association band of δ -valerolactam too, nothing can be said at present. This, as well as the above, is a question yet to be solved.

Discussion on Some General Problems of Molecular Association in Amides.

Some general problems of association in amides will now be discussed. In this field the studies made by A. M. Buswell and his collaborators⁽³⁾ (4) are important. Some of their data, along with the present writer's, are given in Table 3. It is chiefly on these data that the following discussion is based.

Table 3.

3μ region infrared absorptions of amides in CCl_4 solution.

Substances	Wave-lengths of free <i>N-H</i> bands (in μ)		Wave-lengths of <i>N-H</i> association bands (in μ)		Molar absorption coefficients of <i>N-H</i> association bands		Observers
Monosubstituted Amides {	<i>N</i> -Methylacetamide	2.88	2.97 ^(b) →3.03	3.22	0 at 0.0014 mol/l. 9 (2.97 μ) at 0.0032 mol/l.		M. Tsuboi
	<i>N</i> -Ethylacetamide	2.89	2.97 ^(a) →3.03 ^(b)	3.22	6 ^(a) (2.97 μ) at 0.002 mol/l.		A.M. Buswell and others ⁽⁴⁾
	<i>N</i> -Cyclohexylacetamide	2.90	2.97 ^(b) →3.04	3.23	7 (2.97 μ) at 0.002 mol/l.		A.M. Buswell and others ⁽⁴⁾
Unsubstituted Amides {	Acetamide	2.83	2.925	3.03	3.145	17 (3.145 μ) at 0.002 mol/l.	A.M. Buswell and others ⁽³⁾ (4)
	Propionamide	2.83	2.925	3.03	3.15	8 ^(a) (3.03 μ) 14 ^(a) (3.15 μ) } at 0.002 mol/l.	A.M. Buswell and others ⁽⁴⁾
	<i>n</i> -Valeramide	2.83	2.92	3.03	3.14	19 (3.14 μ) at 0.002 mol/l.	A.M. Buswell and others ⁽³⁾ (4)
	Benzamide	2.83	2.925	3.03	3.15	11 ^(a) (3.03 μ) 25 ^(a) (3.15 μ) } at 0.002 mol/l.	A.M. Buswell and others ⁽⁴⁾
δ -Valerolactam		2.92	3.11	3.24	41 (3.11 μ)	at 0.0015 mol/l.	M. Tsuboi

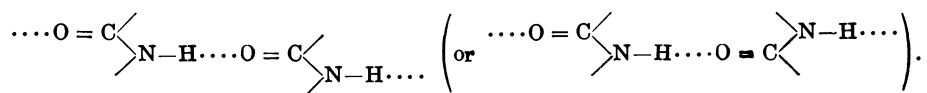
(a) Read from Buswell's curves.

(b) The arrow indicates the shifting of the band on raising the concentration of the solution.

(3) A.M. Buswell, J.R. Dowing and W.H. Rodebush, *J. Am. Chem. Soc.*, **62** (1940), 2759.

(4) A. M. Buswell, W. H. Rodebush, and M.F. Roy, *J. Am. Chem., Soc.*, **60** (1938), 2444.

Structures of Associated Molecules of Amides. *Monosubstituted Amides.* The inspection of Table 3 reveals that *N*-methylacetamide, *N*-ethylacetamide, and *N*-cyclohexylacetamide are closely similar to each other in their 3μ region absorptions in carbon tetrachloride solution. Thus, they are nearly equal with respect to the wave-lengths of N—H absorption bands of free and associated molecules, with respect to the absorption intensities of association bands, and with respect to the shifting of the $2.97 \sim 3.04\mu$ band with concentrations of the solutions. These show that *N*-methylacetamide, *N*-ethylacetamide, and *N*-cyclohexylacetamide are alike in the molecular configurations, both in the single and associated states. In general it may be said that: the molecules of the ordinary monosubstituted amides RCONHR' are of the *trans* form (probably due to the steric repulsion between R and R' in each molecule), and on association they form chain polymers:



Unsubstituted Amides. Unsubstituted amides show N—H association bands at 3.03μ and $3.14 \sim 3.15\mu$. Of these two bands the former is located near the $2.97 \sim 3.03\mu$ band of *N*-methylacetamide and the latter near the 3.11μ band of δ -valerolactam. Moreover, at relatively low concentration (e. g. 0.002 mol/l.) in their carbon tetrachloride solution, the absorption intensity of the $3.14 \sim 3.15\mu$ band of unsubstituted amides is stronger than that of the 3.03μ band; likewise the absorption intensity of the 3.11μ band of δ -valerolactam is stronger than that of the 2.97μ band of *N*-methylacetamide. These facts show that the molecules RCONH_2

associate at first to form ring dimers: $\text{R}-\text{C} \begin{array}{c} \diagup \text{O} \cdots \text{H}-\text{N} \\ \diagdown \text{N}-\text{H} \cdots \text{O} \end{array} \text{C}-\text{R}$ through

double N—H $\cdots$ O bondings (the hydrogen here being that one of the two, which is *cis* to the oxygen in each molecule), and then polymers through single N—H $\cdots$ O bonding (the hydrogen here being the other one of the two).

N. B. The absorption band at $3.11 \sim 3.15\mu$ might be due to the configuration $\text{—C} \begin{array}{c} \diagup \text{O} \cdots \text{H}-\text{N} \\ \diagdown \text{N}-\text{H} \cdots \text{O}=\text{C} \end{array}$ in the ring dimer structure rather than the ring dimer structure itself, for, according to Buswell⁽³⁾, the 3.14μ band is given also by the crystal of acetamide, in which the constituent molecules, as may be seen from the X-ray analysis by F. Senti and D. Harker⁽⁵⁾, are bonded so that the configuration $\text{—C} \begin{array}{c} \diagup \text{O} \cdots \text{H}-\text{N} \\ \diagdown \text{N}-\text{H} \cdots \text{O}=\text{C} \end{array}$ is formed but not the ring dimer structure.

(5) F. Senti and D. Harker, *J. Am. Chem. Soc.*, **62** (1940), 2008.

N-H Stretching Vibrations in the Associated Molecules of Amides.

The above conclusion concerning the relation between the frequencies of N—H stretching vibrations in amides and the configurations of their associated molecules may be summed up in Table 4. It is to be noted that the difference in frequencies of N—H stretching vibrations (in corresponding linkages) between C—CO—NH₂ and C—CO—NH—C is comparatively small.

Table 4.

Frequencies of N-H stretching vibrations	C-CO-NH ₂	C-CO-NH-C
(A) in single N—H...O=C	—	3360 cm. ⁻¹ (2.97 μ)
(B) in $\begin{array}{c} \dots \text{O}=\text{C} \\ \quad \diagdown \\ \quad \text{N}-\text{H} \dots \text{O}=\text{C} \\ \quad \quad \diagdown \\ \quad \quad \text{N}-\text{H} \dots \\ \quad \quad \quad \diagup \\ \quad \quad \quad \text{N}-\text{H} \dots \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N}-\text{H} \dots \text{O}=\text{C} \end{array}$ (or $\begin{array}{c} \dots \text{O}=\text{C} \\ \quad \diagdown \\ \quad \text{N}-\text{H} \dots \text{O}=\text{C} \\ \quad \quad \diagup \\ \quad \quad \text{N}-\text{H} \dots \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N}-\text{H} \dots \end{array}$)	3300 cm. ⁻¹ (3.03 μ)	3360~3280 cm. ⁻¹ (2.97~3.04 μ)
(C) in $\begin{array}{c} \text{O} \dots \text{H}-\text{N} \\ \diagup \quad \diagdown \\ -\text{C} \quad \text{N}-\text{H} \dots \text{O}=\text{C} \end{array}$	3180~3170 cm. ⁻¹ (3.14~3.15 μ)	3210 cm. ⁻¹ (3.11 μ)

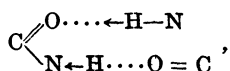
The fact that the frequencies are lower in (B) than in (A), as shown in Table 4, may be explained as follows: In the molecule of an amide, there is an electric polarity due to resonance, $\text{O}=\text{C}-\text{NH}-\leftrightarrow\text{O}^--\text{C}=\text{NH}^+-$. This polarity must increase, if the oxygen of this molecule accepts the hydrogen (or proton) of another molecule, and accordingly the electronegativity of the nitrogen must increase too. Hence, the N—H...O bonding must be stronger in the associated molecules of the polymer (B) than in those of the non-ring type dimer (A), and the N—H bond in the former must be weaker than that in the latter. This explains why the frequencies of N—H stretching vibrations is lower in the former than in the latter.

That the frequencies are lower in (C) than in (B) and (A) (Table 4) may be explained as follows: Let the potential energy V of the system (C) be

$$V = \frac{1}{2} k_1(q_1^2 + q_2^2) + k_2 q_1 q_2,$$

where q_1 and q_2 are the displacements (at a given time) from equilibrium in the stretching vibrations of the two N—H's in the system, the signs of q_1 and q_2 being taken as positive for stretching and as negative for contraction; k_1 the force constant of each N—H; and k_2 the force constant corresponding to the interaction between the two N—H's. Then

we obtain the frequency ν , for the infrared-active vibration:



$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k_1 - k_2}{m}},$$

where m is the reduced mass of N—H. In (C), the Coulomb repulsion between the two hydrogens (or protons) is probably the most effective interaction between the two N—H's. If so, k_2 must be positive, because the stretching of the distance of one N—H in the system (C) tends to contract the distance of the other N—H, while k_2 must be nearly zero in (B) and (A). This explains why the frequencies are lower in (C) than in (B) and (A).

Association Tendencies of Amide Molecules. As is seen from Table 3, δ -valerolactam shows a stronger tendency towards association than unsubstituted amides, both of which are capable of forming the ring dimer. This fact may be explained as follows: In the amide or lactam molecule, the nitrogen atom, positively charged due to resonance, would attract the electrons of the hydrogen atoms and leave the protons bare to be attached to negatively charged oxygen atoms of another molecule. This process would be more effective (per one N—H) in the case where only one hydrogen is on the nitrogen than in the case where two hydro-

gens are on it. Hence, the dissociation energy of $\text{C}-\overset{\text{C}}{\underset{\text{H}}{\text{N}}}-\text{H} \cdots \cdots \text{O}=\text{C}$

bonding must be greater than that of $\text{C}-\overset{\text{H}}{\underset{\text{H}}{\text{N}}}-\text{H} \cdots \cdots \text{O}=\text{C}$ bonding. This explains the difference in association tendencies of the two kinds of molecules.

Buswell and his collaborators⁽⁴⁾ indicated that the monosubstituted amides in general show a smaller tendency towards association than the unsubstituted amides. This difference in association tendencies is, according to the present writer's view, due to the difference in molecular structures of these two kinds of amides, the one, $\text{R}-\overset{\text{R}}{\underset{\text{O}}{\text{C}}}-\text{N} \begin{array}{l} \text{H} \\ \diagup \quad \diagdown \\ \text{R}' \end{array}$, being in-

capable of forming ring dimers, the other, $\text{R}-\overset{\text{R}}{\underset{\text{O}}{\text{C}}}-\text{N} \begin{array}{l} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$, capable. It is rather probable, however, that the dissociation energy per one N—H $\cdots$ O bonding is greater in monosubstituted amides (and lactams) than in unsubstituted amides.

Supplement.

While this paper was in press, the writer made some observations on the infrared absorptions of ϵ -caprolactam $\left(\begin{array}{c} \text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2 \\ \diagdown \quad \diagup \\ \text{CO-NH-CH}_2 \end{array} \right)$, another example of the cyclic compounds with the peptide linkage, and found the following facts: (1) ϵ -Caprolactam shows in its carbon tetrachloride solution the free N-H absorption band at 2.90μ and the N-H association bands at 3.09μ and 3.23μ . (2) ϵ -Caprolactam has a stronger tendency of molecular association than monosubstituted amides, the molar absorption coefficient at 3.09μ of ϵ -caprolactam being as great as 22 even in such a dilute carbon tetrachloride solution as 0.0007 mol/l. (3) No shifting occurs in the positions of the absorption maxima of the N-H association bands with change of the concentration of the solution. These facts show that in the ϵ -caprolactam molecule, as in the δ -valerolactam molecule, H on N is *cis* to O, and that the molecules associate to form ring dimers.

In conclusion the writer wishes to express his sincere thanks to Professor San-ichiro Mizushima and Assistant Professor Takehiko Simanouti for their kind guidance throughout the present work.

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b) *L'action sur l'infusion pleurétique.*

On a dissous 10 c.c. de l'infusion pleurétique dans 50 c.c. de la solution de tampon, a filtré le précipité et ajouté 1 c.c. de la solution des sels du néodyme à plusieurs concentrations à 1 c.c. de ce filtre.

Table 2.

concentration du néodyme après l'ad- dition sel du néodyme %	4	3	2	1	1/2	1/3	1/4	1/6	1/8	1/10	1/16	1/20	1/25	1/50	1/64	1/128
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	—	—	—	—	—	++	##	##	++	+	±	±	±	±	±	—
$\text{Nd}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$	—	—	—	—	—	+	##	##	+	+	±	±	±	±	±	—

c) *L'action sur l'ascite.*

Le même procédé à l'infusion pleurétique.

Table 3.

concentration du néodyme après l'ad- dition sel du néodyme %	4	3	2	1	1/2	1/3	1/4	1/5	1/8	1/10	1/16	1/20	1/25	1/50	1/64	1/128
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	—	—	—	+	++	##	##	##	++	+	+	+	±	±	±	—
$\text{Nd}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$	—	—	—	++	##	##	##	++	++	+	+	+	±	±	±	—

(2) **Analyse du néodyme dans la protéine précipitée et calcul de l'équivalent du néodyme combiné avec 1 g. de la protéine.** On a ajouté la solution des sels du néodyme à la solution de l'albumine d'oeuf à 0.5% (pH 5.6). Après trente minutes, la protéine est séparée par la centrifugation et ayant lavé cette précipitation cinq fois avec de l'eau, on l'a fait sécher dans l'exsiccateur. L'analyse du néodyme a été faite gravimétriquement comme l'oxalate. Le résultat est montré ci-dessous.

Table 4.

sel du néodyme	concentration du néodyme après l'addition. %	Nd % dans la pro- téine précipitée.	équivalent du néodyme combiné avec 1 g. de la protéine ($\times 10^{-5}$)
$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$	1/4	2.11	45
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	1/4	2.44	52
$\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	1/2	2.57	55
$\text{Nd}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$	1/3	2.11	47
$\text{Nd}(\text{C}_2\text{H}_5\text{COO})_3 \cdot \text{H}_2\text{O}$	1/3	2.34	50

Conclusion. (1) Comme on a observé, les sels du néodyme se combinent très fortement avec la protéine et la font précipiter.

(2) La concentration nécessaire pour la précipitation est comme suite.
a—Par la solution bien concentrée du sel, la protéine ne se précipite pas. b—La capacité de la précipitation est maximum pour la concentration moyenne.

(3) L'analyse du néodyme dans la protéine précipitée a montré que l'équivalent combiné avec 1 g. de la protéine est constant dans plusieurs sels du néodyme et sur l'albumine d'œuf cette valeur est approximativement 50×10^{-5} (pH. 5.6).

(4) De ces résultats, on peut dire que l'absorption et l'évacuation sont assez faibles parce que la formation des composés insolubles des sels du néodyme et de la protéine conduit à se déposer dans le système réticulendothérial.

En terminant ce compte rendu de mes recherches, j'ai à exprimer mes sincères remerciements à M. le Prof. Kenjiro Kimura pour les aimables et très utiles indications, ainsi qu' à M. M les Profs. Kéigi Misawa, Taku Uémura, Eiji Ochiai et à Yosoji Ito, et à M. M les Profs. adjoint Kazuo Kuroda et Taro Kawamura, qui ont bien voulu me prêter leurs bienveillants conseils pour mes expériences.

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Fundamental Studies on the Current-Voltage Curve in Polarography. II.*

Derivation of the Activation-Controlled Polarographic Waves of Simple Metal Ions from the Standpoint of Chemical Kinetics.

By Reita TAMAMUSHI and Nobuyuki TANAKA.

(Received March 12, 1949.)

In the previous paper⁽¹⁾ the authors derived the formula of the reversible current-voltage curve from the standpoint of chemical kinetics,

* Presented at the 2nd annual meeting of the Chemical Society of Japan on April 1949.

(1) N. Tanaka and R. Tamamushi, This Bulletin, **22** (1949), 187.

and showed that the polarographic electrode potential can be defined by the Nernst's equation if the rate-determining step of the net electrode process is diffusion. In the present paper the authors analyse the relation between the current flowing and the electrode potential, when the rate-determining step is the activation process at the potential region where the rates of the forward and reverse reactions are nearly the same. By the same treatment as in the case of diffusion-control, some interesting results for the current-voltage relation are obtained. The theoretical curve which is analogous to the usual irreversible current-voltage curve is obtained under these conditions, and the meaning of the half-wave potential of such a wave is set down.

The Derivation of Equations.

Consider the net electrode process which contains the diffusion process and the electron-transfer reaction (the activation process) only. As the oxidation-reduction process, the reaction $M^{m+} + n\varepsilon \rightleftharpoons M^{(m-n)+}$ is considered, in which M^{m+} and $M^{(m-n)+}$ symbolize the oxidant and the reductant, respectively. Let us assume that the reduction is the forward reaction and the oxidation is the reverse. In the absence of any external potential, the rates of the two reactions are represented as follows:

$$\begin{aligned} \text{forward :} \quad & s \frac{kT}{h} e^{-\Delta F_1/RT} \equiv \kappa_1 \\ \text{reverse :} \quad & s \frac{kT}{h} e^{-\Delta F_2/RT} \equiv \kappa_2, \end{aligned} \tag{1}$$

where s is the constant concerning the nature of the electrode surface, ΔF_1 and ΔF_2 are the free energies of activation and κ_1 and κ_2 are the abbreviations of the corresponding terms, respectively. If the particular potential V is applied to the electrode against the interior of the solution, the two rates must be written as follows:

$$\begin{aligned} \text{forward :} \quad & \kappa_1 e^{-\frac{n\alpha VF}{RT}} \equiv \kappa_1 E_1 \\ \text{reverse :} \quad & \kappa_2 e^{\frac{n(1-\alpha)VF}{RT}} \equiv \kappa_2 E_2 \end{aligned} \tag{2}$$

αV is the fraction of the total applied potential V which will promote the forward reaction, and therefore $(1-\alpha)V$ will retard the reverse. If the activities of the oxidant and the reductant at the electrode surface are represented by $[A_o]$ and $[A_r]$, the current flowing by the electrode activation process is expressed by equation (3).

$$I = n\varepsilon \{ \kappa_1 E_1 [A_o] - \kappa_2 E_2 [A_r] \} \tag{3}$$

This current is carried by the diffusion process of oxidant, namely :

$$I = n\varepsilon K_o([C_o]^\circ - [C_o]) = n\varepsilon \frac{K_o}{f_o}([A_o]^\circ - [A_o]) = n\varepsilon K_o'([A_o]^\circ - [A_o]) \quad (4)$$

or by that of reductant, namely :

$$I = n\varepsilon K_R([C_R] - [C_R]^\circ) = n\varepsilon \frac{K_R}{f_R}([A_R] - [A_R]^\circ) = n\varepsilon K_R'([A_R] - [A_R]^\circ) \quad (5)$$

where $[A_o]^\circ$, $[A_R]^\circ$ are the activities of the oxidant and reductant in the body of the solution, $[C_o]$, $[C_R]$, $[C_o]^\circ$, $[C_R]^\circ$ are the concentrations of the oxidant and reductant at the electrode surface and in the body of the solution, and f_o , f_R symbolize the activity-coefficients of the corresponding terms. From equations (3), (4) and (5) the general relation between the current I and the electrode potential V is obtained :

$$I = n\varepsilon \frac{K_o'K_R'(\kappa_1E_1[A_o]^\circ - \kappa_2E_2[A_R]^\circ)}{\kappa_1E_1K_R' + \kappa_2E_2K_o' + K_o'K_R'} = n\varepsilon \frac{[A_o]^\circ - [A_R]^\circ \frac{\kappa_2E_2}{\kappa_1E_1}}{\frac{1}{K_o'} + \frac{1}{\kappa_1E_1} + \frac{1}{K_R'} \frac{\kappa_2E_2}{\kappa_1E_1}} \quad (6)$$

$$= n\varepsilon \frac{[A_o]^\circ \frac{\kappa_1E_1}{\kappa_2E_2} - [A_R]^\circ}{\frac{1}{K_o'} \frac{\kappa_1E_1}{\kappa_2E_2} + \frac{1}{\kappa_2E_2} + \frac{1}{K_R'}} \quad (6')$$

Now let us consider the magnitudes of K_o' , K_R' , κ_1E_1 and κ_2E_2 in equations (6) and (6'). K_o' and K_R' , which depend on the diffusion coefficients of the oxidant and the reductant in the solution, may be generally regarded to be almost identical. On the other hand, κ_1E_1 and κ_2E_2 are the functions of the electrode potential V that is continuously changed in polarography. Therefore, the magnitudes of the above four values should be compared at the particular potential region separately. So, in the present treatment, the total current-voltage curve is divided into three parts according to the value of V , i. e., $\kappa_1E_1 \cong \kappa_2E_2$ (Part A), $\kappa_1E_1 > \kappa_2E_2$ (Part B) and $\kappa_1E_1 < \kappa_2E_2$ (Part C).

Part A of the Current-Voltage Curve. If it is assumed that V equals V_0 when κ_1E_1 just equals κ_2E_2 ; V is nearly equal to V_0 in this potential region. From the condition for the activation-controlled reaction, the following relation is satisfied in this part, i. e.,

$$\kappa_1E_1 \cong \kappa_2E_2 \ll K_o', K_R'. \quad (7)$$

Applying this relation to equation (6) or (6'), the approximate equation of the current-voltage curve in this region can be obtained :

$$I/n\varepsilon = \kappa_1 E_1 [A_o]^\circ - \kappa_2 E_2 [A_R]^\circ \quad (8)$$

From this formula it can be seen that the current flowing at such an electrode potential is determined only by the rates of activation process.

Part B of the Current-Voltage Curve. In this potential region, the more negative the electrode potential V , the greater is the rate of the forward reaction $\kappa_1 E_1$, while the rate of the reverse reaction $\kappa_2 E_2$ tends to be negligibly small.

(a). $\kappa_1 E_1$ becomes almost equal to both of K'_o and K'_R .—Then, $\kappa_2 E_2 / \kappa_1 E_1$ is very small and nearly equal to zero. Therefore, considering these relations, the equation for the current-voltage curve of this region can be derived from equation (6), namely:

$$I/n\varepsilon = \frac{[A_o]^\circ}{\frac{1}{K'_o} + \frac{1}{\kappa_1 E_1}} = \frac{K'_o \kappa_1 E_1 [A_o]^\circ}{K'_o + \kappa_1 E_1} \quad (9)$$

(b). $\kappa_1 E_1$ is greater than both of K'_o and K'_R .—In this case, obviously, $\kappa_2 E_2 / \kappa_1 E_1$ tends to zero. Hence, from equation (6) the equation

$$I = n\varepsilon K'_o [A_o]^\circ = n\varepsilon K_o [C_o]^\circ \equiv (I_a)_o \quad (10)$$

is obtained, which represents the limiting case and corresponds to the limiting current in polarography.

From equations (9) and (10), it can be said that at Part B-(a) the current is dependent on the characters of the oxidant, but it is independent of those of the reductant, and that Part B-(a) corresponds to the reduction wave of the polarographic wave. Furthermore, the limiting current of such a case is expected to be defined by the Ilkovič's equation.

Part C of the Current Voltage Curve. In this region the rate of the reverse reaction increases as the electrode potential V is going to be more positive than V_0 , while the rate of the forward reaction decreases to a negligibly small value. By the same treatment as for Part B, the equations for the anodic wave and the anodic limiting current are obtained from equation (6') as follows:

(a). $\kappa_2 E_2$ becomes almost equal to both of K'_o and K'_R .

$$I/n\varepsilon = -\frac{[A_R]^\circ}{\frac{1}{K'_R} + \frac{1}{\kappa_2 E_2}} = -\frac{K'_R \kappa_2 E_2 [A_R]^\circ}{K'_R + \kappa_2 E_2} \quad (11)$$

(b). $\kappa_2 E_2$ is greater than both of K'_o and K'_R .

$$I = -n\varepsilon K'_R [A_R]^\circ = -n\varepsilon K_R [C_R]^\circ \equiv (I_a)_R \quad (12)$$

These equations (8), (9), (10), (11) and (12) are expected to account for the total wave of oxidation-reduction process which proceeds at the polarographic electrode under the conditions above described.

Theoretical Analysis of the Curve.

In the following, the meaning of the half-wave potential, the tangent of the curve and the other important properties of the curve will be described in relation to the equations derived above.

The Electrode Potential where the Current is Equal to Zero. In Part A of the current-voltage curve there must be such a point where the current flowing is zero, i. e., $I = 0$. From equation (8) the relation between the electrode potential and the activities of the oxidant and the reductant in the body of the solution can be easily obtained as follows:

$$\left[\frac{\kappa_2 E_2}{\kappa_1 E_1} \right]_{I=0} = \frac{[A_o]^\circ}{[A_R]^\circ} \quad (13)$$

or

$$[e^{n(V-V_0)F/RT}]_{I=0} = \frac{[A_o]^\circ}{[A_R]^\circ}$$

in which the condition, $I = 0$, is satisfied. That is to say, the potential V , under the condition $I = 0$, may be determined only by the activities $[A_o]^\circ$ and $[A_R]^\circ$, and, furthermore, if $[A_o]^\circ$ is equal to $[A_R]^\circ$, this potential will represent the normal oxidation-reduction potential of the system. Therefore, if $[A_o]^\circ$ and $[A_R]^\circ$ are known and the potential $[V]_{I=0}$ are determined from the experimental curve, the normal oxidation-reduction potential V_0 can be obtained from the experimental result. In practice, since, in this potential region, the current flowing is usually very small and the inclination of the curve at the point $[V]_{I=0}$ is also very small as shown later, it will be somewhat difficult to determine the correct value of V_0 by this method.

Half-Wave Potential. There are two half-wave potentials in the total current-voltage curve, i. e., the half-wave potentials of the cathodic part and the anodic part. First, the relations for the cathodic half-wave potential will be derived, and then for the anodic one in the same way.

By substituting $(I_a)_o$ for $n\epsilon K'_o[A_o]^\circ$ of equation (9), the equation,

$$\kappa_1 E_1 = \frac{K'_o I}{(I_a)_o - I} \quad (14)$$

or

$$V = -\frac{RT}{n\alpha F} \left(\frac{\Delta F_1}{RT} + \ln \frac{h}{kT} K'_o + \ln \frac{I}{(I_a)_o - I} \right),$$

is obtained. At the half-wave potential the current flowing is one half of the limiting current $(I_a)_o$, namely:

$$I = \frac{(I_a)_o}{2} \quad (15)$$

From equations (14) and (15) the condition for the cathodic half-wave potential is derived as follows:

$$[\kappa_1 E_1] \frac{(I_a)_o}{2} = K'_o \quad (16)$$

or

$$[V] \frac{(I_a)_o}{2} = -\frac{RT}{n\alpha F} \left(\frac{\Delta F_1}{RT} + \ln \frac{h}{kT} K'_o \right) \quad (16)$$

The equation (16) shows that the half-wave potential depends on the constant K'_o , and that if the value of α is independent of the activity of the oxidant, it will be the particular constant for the oxidant concerned.

As for the anodic half-wave potential analogous equations can be obtained, i. e.,

$$[\kappa_2 E_2] \frac{(I_a)_R}{2} = K'_R \quad (17)$$

or

$$[V] \frac{(I_a)_R}{2} = \frac{RT}{n(1-\alpha)F} \left(\frac{\Delta F_2}{RT} + \ln \frac{h}{kT} K'_R \right) \quad (17)$$

The Relation between $\log(I/I_a - I)$ and V . From equations (14) and (17) it is obvious that the relation between $\log(I/I_a - I)$ and V must be linear and the absolute value of the tangent of this line is $RT/n\alpha F$ or $RT/n(1-\alpha)F$ according to the cathodic or anodic part. If this relation is plotted and the tangent of the line is determined, the value of α can be calculated. Although many investigators have often used this linear relation for the criterion of reversibility of polarographic wave, it is obvious that this may hold also in such a case when the electrode potential is not defined by the Nernst's equation. In the case when the oxidation-reduction reaction concerned is uni-valent, if the wave is reversible, the theoretical inclination of the above relation must be 0.059 volt at 25°C, hence, if the experimental result deviates from this value, we may conclude that the electrode activation process does not exist in an equilibrium state.

Index Potential $V_i^{(2)}$. In the potentiometric study of the oxidation-reduction systems the term "index potential" has been used to specify the types of the titration curve. A similar quantity has been applied

to analyse the type of polarographic wave. As the index potential V_i of the polarographic wave the quantity,

$$V_i = [V]_{\frac{3I_d}{4}} - [V]_{\frac{I_d}{2}} \quad \text{or} \quad [V]_{\frac{I_d}{2}} - [V]_{\frac{I_d}{4}}^{(3)} \quad (18)$$

is given, where $[V]_{\frac{3I_d}{4}}$ and $[V]_{\frac{I_d}{4}}$ are the potentials at which the wave-heights are $3I_d/4$ and $I_d/4$ respectively. From equation (9) the condition for $[V]_{\frac{I_d}{4}}$ of the cathodic part is to be

$$[\kappa_1 E_1]_{\frac{I_d}{4}} = \frac{K'_o}{3} \quad (19)$$

or

$$[V]_{\frac{I_d}{4}} = -\frac{\Delta F_1}{n\alpha F} - \frac{RT}{n\alpha F} \ln \left(\frac{h}{kT} \frac{K'_o}{3} \right) .$$

Subtracting equation (19) from equation (16) and rearranging, equation (20) is obtained, by which the value of α can be calculated.

$$\alpha = \frac{RT}{nF} \frac{\ln 3}{[V]_{\frac{I_d}{4}} - [V]_{\frac{I_d}{2}}} = \frac{0.059}{n} \frac{0.477}{[V]_{\frac{I_d}{4}} - [V]_{\frac{I_d}{2}}} \quad (20)$$

This method of calculation of α is essentially identical with the method described above. However, the accuracy of this method is lower than the previous method, because equation (20) utilizes only two particular points of the experimental curve, while the previous method uses a series of points of the curve to determine α .

First Derivative of the Current-Voltage Relation.—Tangent of the Curve. Differentiating the equations (8), (9) and (11) with respect to the electrode potential V , the tangents of the curves of Parts A, B and C are represented as follows:

$$\text{Part A} \quad \frac{dI}{dV} = -n\varepsilon \frac{nF}{RT} \{ \alpha [A_o]^\circ \kappa_1 E_1 + (1-\alpha) [A_R]^\circ \kappa_2 E_2 \} \quad (21)$$

$$\text{Part B} \quad \frac{dI}{dV} = -n\varepsilon \frac{nF}{RT} \alpha K'_o \kappa_1 E_1 \frac{K'_o [A_o]^\circ}{(K'_o + \kappa_1 E_1)^2} \quad (22)$$

$$\text{Part C} \quad \frac{dI}{dV} = -n\varepsilon \frac{nF}{RT} (1-\alpha) K'_o \kappa_2 E_2 \frac{K'_o [A_R]^\circ}{(K'_o + \kappa_2 E_2)^2} \quad (23)$$

From equations (13) and (21) the tangent of the curve at the point $I = 0$ can be obtained.

(3) R. Brdicka, *Z. Electrochem.*, **47** (1941), 314.

$$\left[\frac{dI}{dV} \right]_{I=0} = -n\varepsilon \frac{nF}{RT} [A_o]^\circ \kappa_1 E_1 \quad (24)$$

The tangent at the cathodic half-wave potential is derived by the application of equation (16) to equation (22):

$$\left[\frac{dI}{dV} \right]_{\frac{U_{d.o.}}{2}} = -n\varepsilon \frac{nF}{4RT} \alpha \kappa_1 E_1 [A_o]^\circ = -n\varepsilon \frac{n\alpha F}{4RT} K'_o [A_o]^\circ \quad (25)$$

Now let us compare the two tangents (24) and (25) with each other. Dividing (25) by (24), equation (26) is obtained as follows, unless the value of α is very small:

$$\frac{\left[\frac{dI}{dV} \right]_{\frac{U_{d.o.}}{2}}}{\left[\frac{dI}{dV} \right]_{I=0}} = \frac{\alpha K'_o}{4[\kappa_1 E_1]_{I=0}} > 1 \quad (26)$$

From the result, it can be said that the cathodic wave is far steeper than the wave of part A. The same relations are to be held with between the anodic wave and the wave of Part A.

Second Derivatives of the Current-Voltage Relation.—Inflection Point of the Curve. By deriving the second derivatives of equations (8), (9) and (11) with respect to the electrode potential V and by making these derivatives equal to zero, the inflection points of the current-voltage curves are obtained. The three following relations are obtained for the conditions of the inflection points of the waves, i. e.,

$$\text{Part A} \quad \left[\frac{\kappa_2 E_2}{\kappa_1 E_1} \right]_{\text{infl. pt. A}} = \frac{\alpha^2}{(1-\alpha)^2} \frac{[A_o]^\circ}{[A_R]^\circ} \quad (27)$$

$$\text{Part B} \quad [\kappa_1 E_1]_{\text{infl. pt. B}} = K'_o \quad (28)$$

$$\text{Part C} \quad [\kappa_2 E_2]_{\text{infl. pt. C}} = K'_R \quad (29)$$

It is pointed out from these equations that the inflection point of cathodic or anodic wave is identical with the corresponding half-wave potential. Consequently it is concluded that there may be three inflection points in the total region of the polarographic oxidation-reduction wave.

The Tracing of the Theoretical Curve Using the Equations Derived Above. As an example, let us assume some hypothetical values of ΔF_1 , ΔF_2 , α , $[A_o]^\circ$, $[A_R]^\circ$, K'_o and K'_R as follows, and trace the theoretical curve according to the obtained equations (8), (9) and (11) (Fig. 1).

$$\Delta F_1 = 15.0 \times 10^4 \text{ joule,}$$

$$\Delta F_2 = 13.1 \times 10^4 \text{ joule,}$$

$$[A_o]^\circ = [A_R]^\circ = 1.04 \times 10^{-3} \text{ mol/l.,} \quad K'_o = K'_R = 1.8 \times 10^{-8} \text{ amp./mol/l.,}$$

$$\alpha = 0.6,$$

$$n = 1.$$

Under these conditions the following values are obtained for $[V]_{\frac{(U_d)_o}{2}}$, $[V]_{\frac{(U_d)_R}{2}}$ and $[V]_{I=0}$, i. e.,

$$[V]_{\frac{(U_d)_o}{2}} = -0.569 \text{ volt vs. hydrogen electrode.}$$

$$[V]_{\frac{(U_d)_R}{2}} = +0.353 \text{ ,, ,, ,, ,,}$$

$$[V]_{I=0} = -0.200 \text{ ,, ,, ,, ,,}$$

From Fig. 1 it can be said that the theoretical curve is essentially the same, at least qualitatively, as some types of irreversible waves obtained in polarography, and that the equations cited above will account for the natures of the polarographic waves which have not yet been interpreted.

Summary.

In this paper the authors have derived the equations of the polarographic current-voltage curve from the standpoint of chemical kinetics, assuming that the net electrode process is activation-controlled. The results obtained are summarized as follows:

(1) Half-wave potential is the constant of the substance concerned, and is independent of its activity.

(2) The potential where the current is equal to zero is only defined by the activities of the oxidant and the reductant in the body of the solution.

(3) The inflection point of the cathodic or anodic wave agrees with its half-wave potential.

(4) The relation between $\log(I/I_d - I)$ and V of the cathodic or anodic wave is a straight line.

(5) The values of ΔF_1 , ΔF_2 and α are possible to be calculated from the experimental data.

(6) The theoretical curve is essentially the same as the experimental curve of the irreversible type.

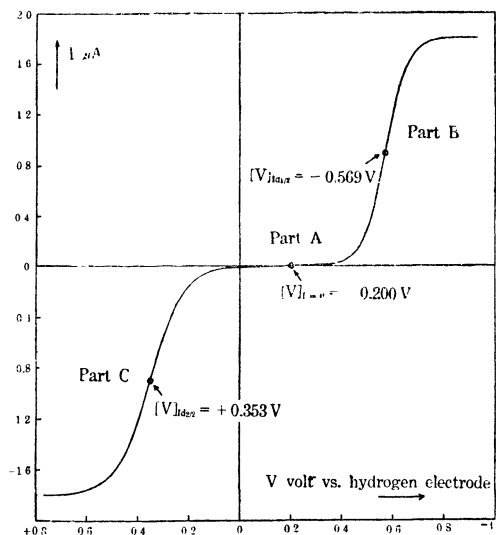


Fig. 1. Theoretical Curve.

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The Determination of Thallium in Flue-Dust and Lead Chamber Muds.

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Introduction. Thallium is one of the rare elements found as an essential constituent in any substantial quantity in only two or three minerals. But in small proportions thallium is widely distributed in natural rocks and minerals such as carnalite, alunite, copper and iron sulphide, zinc blend and braunite. When they are used as in industries, thallium is concentrated in chamber muds and flue-dust giving rise to a determinable amount. Thus thallium is more usually found accumulated in these substances rather than as a constituent of minerals.⁽¹⁾

Thallium was discovered spectroscopically in chamber muds by Crookes and Lamy⁽²⁾ independently in 1861. Since then various workers had succeeded in determining the thallium content in both chamber muds and flue-dust.

When the determination of thallium content in such samples was undertaken for the purpose of securing the most abundant technical source of the element, the author reviewed the methods applied hitherto. But they were found to be unsatisfactory in some respects from the reason that they require an elaborate process of separation due to the

(1) W. T. Roepper, *Am. Jour. Science*, (2), **35** (1863), 421; R. Böttger, *Lieb. Ann.*, **126** (1863), 177, 266; F. Wöhler, *Lieb. Ann.*, **142** (1867), 263; T. Carstanjen, *J. Prakt. Chem.*, **102** (1867), 65; N. N. Melnikow, *Uspeki. Chim.*, **4** (1935), 256; A. V. Petar, *U. S. Bur. Mines Information*, circular No. **6453** (1931), 31.

(2) W. Crookes, *Chem. N.*, **3** (1861), 193, 303; *J. Chem. Soc.*, **17** (1864), 115; *Chem. N.*, **7** (1863), 133; A. Lamy, *Compt. rend.*, **54** (1862), 1255; *Lieb. Ann.*, **124** (1862), 215.

presence of many metals, such as copper, iron, zinc and lead, etc., occurring in quantities hundreds and thousands times greater than thallium.

However, among these methods proposed up to the present date the one suggested by Spacu and Pope⁽³⁾ appeared to be the most effective and an improvement upon it was successfully undertaken by the author as was already described in detail in a previous report.⁽⁴⁾

Thus a minute amount of thallium as slight as 0.001% can be determined by this improved method with fairly good results. The results obtained from about 45 samples of chamber muds and flue-dust collected from sulfuric acid plants and refineries in Japan are described in this report.

Experiment. (a) Moisture: Moisture content was determined by placing a sample in original state in an air oven for 2 hours and drying at 105°C. Several samples were hygroscopic after drying, probably owing to the presence of free sulfuric acid.

(b) Color: The color of a sample was compared with the soil color table published by Japan Forestry Society in accordance with the National Color Standard.

(c) Specific gravity: The specific gravity is determined by measuring the sample already dried (105°C) with a pycnometer.

(d) Thallium determination: This determination has already been given in detail by the author in a previous report but will be briefly recorded in the following. According to the amount of thallium content to be expected in the sample, approximately 30 g. to 50 g. of the dried powdered sample is taken and dissolved by heating with an acid mixture, consisting of one part of H₂O, two parts each of HCl and HNO₃ and four parts of H₂SO₄, being mixed in the order named.

Heating is continued until all traces of copious sulfur dioxide fumes have ceased to appear. The residual cake is disintegrated with 1 N hot sulfuric acid solution, to which it is preferable that a few drops of H₂O₂ is added to reduce any Tl⁺⁺⁺ that may have been formed in the process. After standing for a few minutes this is thoroughly extracted and neutralized first with sodium hydroxide followed by sodium carbonate solution until carbon dioxide has not been evolved.

Next, sulfur dioxide is passed through the solution until it cools. After filtration the filtrate is heated to boiling to expel sulfur dioxide and acidified to about 1 N hydrochloric acid. Particles of potassium chlorate are added and then 0.5 g. of ammonium chloride, the addition of which is effective in determining a minute amount of thallium. Heating is continued until the filtrated solution is boiled down to half its bulk.

If saturated cobalti-hexammine trichloride solution is added after cooling and filtering, a heavy orange yellow precipitate of Co(NH₃)₆(TlCl₆) will instantaneously appear.

This precipitate is pure enough to be weighed on a glass filter (G4, for fine precipitate), assured to constant weight, after it has been washed thoroughly with 2% HCl solution followed by three times each of 5 ml. 95% alcohol and 5 ml. ether and dried at 105°C. Thallium content is calculated from the following equation:

$$\text{Tl (\%)} = \frac{\text{Weight of precipitate} \times 0.35346}{\text{Weight of sample taken}} \times 100 (\%)$$

(e) Reproducibility: The spectroscopic analysis shows that flue-dust and chamber muds contain a large amount of diverse metals, for example, such as the following:

No. 1. Zn, Cu, Pb, Fe, As, K (major), Ca, Al, Na, Si, Ti, Bi, Mg, Tl, Ge, Cd, Sb, Ag, Ni, Mo (minor).

(3) G. Spacu and A. Pope, *Z. anal. Chem.*, **102** (1940), 322.

(4) Y. Murakami, *This Bulletin*, **22** (1949), 206.

No. 2. Fe, Zn, Ca, Al, Pb, Sb, Mg, Si, Cu, As (major), Bi, Tl, Ba, Sn, K, Na, Sb, Si, In, Ge, Ag, Ti, Co, Cd, Mn.

No. 3. Zn, Pb, Sn, K, Na, Sb, As (major), Tl, Fe, In, Ca, Al, Ag, Cu, Cd, Mo, Mg, Bi, Si.

The interference of these metals in the determination of thallium had been thoroughly tested as already reported and no fatal interference has been observed. To ascertain the reproducibility of this method, three main samples of flue dust were selected for this test upon reference to the results obtained from the spectroscopic test and a known amount of thallium was added to the samples. Thallium was determined by the newly proposed method and the result is shown in Table 1.

Table 1.
Reproducibility

Sample	Thallium added (g.)	Thallium complex (g.)	Thallium found (g.)	Thallium calculated (g.)	Difference (g.)
1. Flue-dust abundant in copper	$\Delta 0.01149$	0.0202 0.0530	0.00714 0.01873	$\Delta 0.01863$	$\Delta +0.00010$
2. Flue-dust abundant in iron	$\Delta 0.01149$	0.0255 0.0581	0.00901 0.02054	$\Delta 0.02050$	$\Delta +0.00004$
3. Flue-dust abundant both in copper and iron	$\Delta 0.01149$	0.0171 0.0497	0.00604 0.01761	$\Delta 0.01753$	$\Delta +0.00008$

Complete satisfaction was obtained from this method: first, it is not hazardous owing to the unnecessary of a preliminary separation of metals: secondly, it is most successfully effective in the determination of small quantities of thallium as little as 0.01%: and thirdly, the results obtained show a minimum average deviation, being less than 1%.

Results. The object was to determine the minute amounts of thallium in 46 samples of flue-dust and chamber muds collected from sulfuric acid plants, fertilizer factories and refineries in Japan. The results are shown in Table 2.

Table 2.
Thallium content in flue-dust and chamber muds

No.	Company	Factory	Moisture (%)	Sp. gr.	Thallium content (%)	Remarks
1	Dainippon Kogyo	Hasei Kogyo	10.44	4.65	0.105	
2	Sumitomo Met. Ind. Co., Ltd.	Gensan Factory	1.23	0.70	0.089	Cottrell dust
3	Nitto Chem. Ind. Co., Ltd.	Yokohama Factory	4.54	3.39	0.042	Cottrell dust
4	Konoshima Chem. Ind. Co., Ltd.	Konoshima Factory	4.04	3.44	0.120	
5	Nippon Soda Ind. Co., Ltd.	Aizu Factory	3.59	3.47	0.016	Cottrell dust
6	Asahi Chem. Ind. K.K.	---	0.52	2.09	0.025	
7	Nippon Kogyo K.K.	Saganoseki Refinery	3.87	2.10	0.169	Cottrell dust

Table 2. (continued.)

No.	Company	Factory	Moisture (%)	Sp. gr.	Thallium content (%)	Remarks
8	Nitto Ryuso K.K.	Tokyo Factory	6.84	3.18	0.021	
9	Toa Kagaku Seiren K.K.	Osaka Factory	9.97	3.12	0.038	Cottrell dust
10	Nippon Jukagaku K.K.	—	2.97	3.08	0.000	
11	Nippon Hydrogen Ind. Co., Ltd.	Onahama Factory	8.14	2.86	0.115	Cottrell dust
12	Nippon Kogyo K.K.	Toyama Factory	3.05	3.05	0.227	Cottrell dust
13	Showa Denko K.K.	Kawasaki Factory	9.61	3.57	0.281	Sulfide ore
14	Nitto Ryuso K.K.	Niigata Factory	7.62	2.98	0.000	
15	Niigata Sulfuric Acid Co., Ltd.	Niigata Factory	9.15	4.15	0.029	Cottrell dust
16	Sansei Kogyo K.K.	Choko Refinery	2.38	4.49	0.031	Chimney dust
17	Teikoku Kohatsu K.K.	Murakami Refinery	1.12	5.33	0.023	Dust chamber
18	Toa Kogyo K.K.	Osaka Factory	5.58	3.54	0.059	
19	Ishihara Kogyo K.K.	Yokkaichi Factory	13.92	5.98	0.010	Smelting furnace
20	Nippon Kogyo K.K.	Chinnanbo Refinery	1.37	0.80	0.074	
21	Nippon Kogyo K.K.	Nagoya Factory	6.76	3.42	0.062	Sulfide ore
23	Furukawa Min. Ind. Co., Ltd.	Nagamatsu Factory	1.67	1.26	0.020	Chamber muds
25	Nippon Kogyo K.K.	Ouji Factory	3.48	3.46	0.006	Sulfide ore (Osaruzawa)
26	Nippon Kogyo K.K.	Ouji Factory	7.43	3.58	0.040	Sulfide ore (Hitachi)
27	Nippon Kogyo K.K.	Ouji Factory	5.23	2.87	0.010	Sulfide ore (Hitachi and Matsuo)
28	Nippon Kogyo K.K.	Chinnanbe Refinery	1.38	0.71	0.012	Hourin mine
29	Mitsui Min. Ind. Co., Ltd.	Nihi Refinery	4.70	1.21	0.091	
30	Sumitomo Min. Ind. Co., Ltd.	Kunitomi Refinery	8.11	0.63	0.007	
32	Nitchitsu Kogyo Kaihatsu K.K.	Konan Refinery	1.90	2.70	0.084	Copper ore
33	Tohoku Hiryo K.K.	Akita Factory	7.05	3.68	0.005	Chamber muds
34	Mitsubishi Kogyo K.K.	Osaruzawa Refinery	6.31	1.76	0.073	
35	Nitto Ryuso K.K.	Shimonoseki Factory	33.86	1.06	0.006	Chamber muds
36	Kureha Boseki K.K.	Nishiki Factory	12.32	3.24	0.053	Sulfuric acid plant

Table 2. (*continued.*)

No.	Company	Factory	Moisture (%)	Sp. gr.	Thallium content (%)	Remarks
41	Fujita Min. Ind. Co., Ltd.	Kosaka Factory	2.56	3.54	0.003	Smelting Furnace
42	Fujita Min. Ind. Co., Ltd.	Kosaka Factory	17.93	4.78	0.104	Converter Furnace
43	Yahagi Chem. Ind. Co., Ltd.	Nagoya Factory	3.75	3.48	0.019	
44	Niigata Sulfuric Acid Ind. Co.	Yokohama Factory	5.65	3.22	0.001	Cottrell dust
45	Nitto Chem. Ind. Co., Ltd.	Nakagawa Factory	4.96	3.85	0.033	Sulfuric acid plant (contact process)
46	Nakagawa Chem. Ind. Co., Ltd.	Nakagawa Factory	6.87	3.52	0.000	Sulfuric acid plant (lead chamber)
47	Toyo Koatsu Kogyo K.K.	Omuda Factory	2.10	1.74	0.002	Hot Cottrell dust
48	Toyo Koatsu Kogyo K.K.	Omuda Factory	4.82	4.41	0.064	Mist Cottrell dust
49	Mitsubishi Min. Ind. Co., Ltd.	Hosonokura Refinery	3.04	1.33	0.039	Cottrell dust (lead)
52	Tagi Seihijo Co., Ltd.	—	17.44	1.33	0.040	Sulfuric acid plant
53	Tagi Seihijo Co., Ltd.	—	21.69	2.92	0.046	Sulfuric acid plant
60	Nitchitsu Kogyo Kaihatsu K.K.	Konan Refinery	1.19	1.38	0.033	Cottrell dust (lead)
61	Mitsubishi Min. Ind. Co., Ltd.	Hosonokura Refinery	6.24	3.66	0.070	Zinc ore

Conclusion. The spectroscopic detection of minute quantities of thallium in the flue-dust and chamber muds was frequently undertaken by several workers but its chemical determination was rare. And in the latter case, the thallium content determined chemically had been exceedingly large,⁽¹⁾ a thing which seldom occurs. For instance in one of the results a value as large as 6% had been reported. Such minute quantities of thallium as determined chemically by the author is impossible to be determined with any other method used hitherto.

Reasons for the superiority of the author's method responsible for the good result are attributed to the following: (1) Preliminary separation is unnecessary upon treatment with sulfuric acid and sulfur dioxide: (2) Moreover the complete and instantaneous precipitation of a minute quantity of thallium as $\text{Co}(\text{NH}_3)_6(\text{TiCl}_6)$ is made possible by the addition of ammonium chloride. Furthermore, this method is most remarkably accurate owing to its small factor of thallium as compared with any

(5) R. Böttger, See foot-note (1); T. Carstanjen, See foot-note (1); T. Carstanjen and Marquart, *Verh. Naturhist. Vereins. Rousz. Rheinlands Westfalens*, **24** (1867), *Correspondenzblatt* S 102; D. Playfair, *Chem. N.*, **39** (1879), 245; A. V. Petar, See foot-note (1).

other factor used hitherto. For example, it is smaller than a half of the factor in the chromate method (0.77895) which had been hitherto the most widely used. Data concerning the locality of these samples and the occurrence of the ores used in these factories were destroyed during the war. Every effort was made since to obtain as full and as complete information as possible regarding these matters but with little success. Though it may not be perfect, an attempt is being made to revive the result obtained from the data.

(1) Thallium Content: The greater part of the samples analysed contained less than 0.05% for each, the total amounting to approximately 67%. Only three samples No. 7, No. 12, No. 13, are extraordinarily rich in thallium, but such a large amount as has been reported by former workers can not be found. No. 12 and No. 13 were chamber muds from pyrites burnt in a sulfuric acid factory. But the nature of the pyrites is not definite owing to data having been lost. The flue-dust used for sample No. 7 was sent from Saganoseki Refinery, one of the largest and oldest refineries in Japan, producing zinc and lead.

(2) Relation between thallium content and specific gravity: There are no samples whose specific gravity lies between 2.1 and 2.9. Therefore these samples can be divided into the two following groups according to specific gravity: Group A, less than 2.1 and Group B, larger than 3.0. The former occurs mostly in flue-dust and the latter, strictly in chamber muds from the sulfuric acid factory. The total content of thallium in almost all the samples, 62% of the whole, is each less than 0.05%. Samples with thallium content larger than 0.05 are as follows: Group A—No. 2, No. 7, No. 20, No. 29, No. 34; Group—B No. 1, No. 4, No. 11, No. 12, No. 13, No. 18, No. 21, No. 32, No. 36, No. 40, No. 42, No. 45, No. 48, No. 61.

Among these groups A and B, No. 7, No. 12, and No. 13 are remarkably abundant in thallium.

(3) Color and Thallium Content: A distinct relation between color and thallium content cannot be observed. However the color of a sample belonging to Group B is dull brown, sepia, chocolate tinged, while on the other hand Group A is dark olive, smoke grey tinged. Carstenjen had reported that red-tinged samples are richer in thallium than grey-tinged samples. Similar conditions may be said of this case also.

The author wishes to express his sincere appreciation to Prof. K. Kimura for his suggestion of the problem and his continued supervision through the investigation. He is also indebted to Miss F. Ueda who has kindly undertaken to perform a part of the experiment.

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(5) The Structure of the Resin Column.⁽²⁾ A burette (B) is cut about 20 cm. long, in the bottom of which well-washed glass-wool is packed (0.5 cm. in thickness). Upon the glass-wool the cation-exchange resin (20 meches) is poured together with distilled water. (The apparent volume of resin layer is 10 c.c. in water). (The existence of bubbles in it should be avoided.) By means of a thin rubber-tube (C), the bottom of the burette is connected with a thin glass-tube (D) as shown in Fig. 1. The other end of the glass-tube is placed 0.5 cm. higher than the top of the resin layer in order to keep the solution level above the resin. Under it a beaker (E) is placed to collect the effluent. Upon the burette (B) a separating funnel (A) is placed so that the sample solution and washings may drop on the resin column.

With such an apparatus, when the velocity of dropping is properly adjusted, the solution passes through the resin column at a constant rate.

(6) Method for Regeneration of the Resin. Add 1 N to 3 N hydrochloric acid to the resin in a beaker, then, after leaving them about 1 hour under occasional stirring, decant out the acid, wash with distilled water, and repeat these processes several times, thus the resin is almost perfectly washed. The resin thus obtained is put into the apparatus with distilled water, and washed perfectly by passing 500 c.c. of the acid and 500 c.c. of distilled water through it. In some cases, it is permitted to wash directly in the apparatus without treating it previously in the beaker.

(7) Method for Saturating the Sulfonic Group with H^+ . The sulfonic group of the resin treated as suggested in (6) is completely saturated with H^+ , and of course phenolic-OH group also remains in the form of OH.

(8) Method for Saturating Only the Sulfonic Group with Na^+ or NH_4^+ . Wash the resin in a beaker as mentioned in (6), pour 1 N sodium chloride solution (pH , if necessary, is moderated about 7 with sodium hydroxide), or 1 N ammonium chloride solution (pH , also about 7 with ammonium hydroxide) into the beaker, and stir the resin thoroughly. After decantation, wash the resin twice with distilled water, add again 1 N sodium chloride solution (pH , about 7) or ammonium chloride solution (pH , about 7), and leave it for hours under occasional stirring.

Then, transfer the resin to the apparatus, pass 300-500 c.c. of 1 N sodium chloride or 1 N ammonium chloride solution (pH , about 7) through it, and then wash it with 500 c.c. of distilled water.

(9) Method for Saturating Both Sulfonic Group and Phenolic-OH Group with Na^+ or NH_4^+ . By using alkaline solution of 1 N sodium chloride (pH , 10-12, with sodium hydroxide) or alkaline solution of 1 N ammonium chloride (pH , 10-12 with ammonium hydroxide), not only in the sulfonic group but also in the phenolic-OH group H^+ is exchanged with Na^+ or NH_4^+ .

Therefore, if above-mentioned alkaline solution of 1 N sodium chloride or 1 N ammonium chloride is passed through the resin column till the pH of effluent becomes equal to that of the poured solution, not only sulfonic group but also phenolic-OH group of the resin is saturated with Na^+ or NH_4^+ .

(10) Notations of the Resin Column. For convenience' sake, the resin columns are described by the following notations:

Cation-Exchange Resin (Phenol-sulfonic acid type): C
 Cation-Exchange Resin, when all groups remain H^+ : CHH
 Cation-Exchange Resin, when only sulfonic group
 is saturated with NH_4^+ : CNH_4H

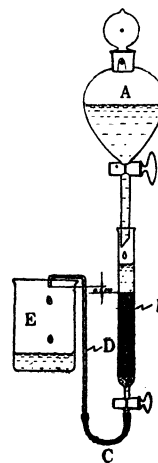


Fig. 1.

(2) Similar apparatus had been used by K. Helrich and W. Rieman III. (*Anal. Chem.*, 19(1947), 651).

Cation-Exchange Resin, when only sulfonic group is saturated with Na^+	: C^{NaH}
Cation-Exchange Resin, when all groups are saturated with NH_4^+	: $\text{C}^{\text{NH}_4^+ \text{NH}_4^+}$
Cation-Exchange Resin, when all groups are saturated with Na^+	: C^{NaNa}

Preparation of Vanadium Standard Solutions.

The standard solution of vanadium (600r V/c.c.) was prepared with ammonium metavanadate (E. Merck). It was standardized with normal solution of potassium permanganate after reducing it with sulfur dioxide (the excess of sulfur dioxide was expelled with carbon dioxide). Thus, 600r of V/c.c. was decided. Then solutions containing 60r/c.c., 6.0r/c.c. and 0.6r/c.c. were prepared. Similarly, the solutions of 261r/c.c., 26.1r/c.c., 13.1r/c.c., 6.5r/c.c. and 3.3r/c.c. were also prepared.

Experiment I. Quinquevalent Vanadium Ion Exchange in C^{III} .

Vanadium solutions of various concentrations and pH (pH was adjusted with ammonium hydroxide and hydrochloric acid) were passed through C^{III} in this experiment. In each case, after passing the sample solution, 100 c.c. of distilled water was passed for washing (flow rate was 1.5 c.c./min.⁽³⁾ and nearly the same in all the following experiments), effluent was gathered in a beaker, alkalized with ammonium hydroxide, concentrated to proper volume by heating on a water-bath, and neutralized with 0.2 N sulfuric acid using methyl orange as indicator after transferring the solution into a separating funnel. Then, vanadium in it was colorimetrically determined by the oxine-chloroform method⁽⁴⁾ using the Pulfrich Stufen Photometer (Zeiss). The results are shown in Table 1.

Table 1.

Experiment number		1	2	3	4	5	6
Sample solution	pH	1.0	5.0	7<	7<	7<	12.0
	Amount of V { r/c.c.	0.6	1.2	1.2	6.0	6.0	0.6
	Total amount (r)	60.0	60.0	60.0	60.0	60.0	60.0
	Total volume (c.c.)	100.0	50.0	50.0	10.0	10.0	100.0
Amount of washings (c.c.)		100	100	100	100	100	100
V, found in effluent (r)		0	0	0	0	0	0

As obviously shown in Table 1, quinquevalent vanadium is completely captured by C^{III} independently of pH of the solutions. Therefore, C^{III} cannot be used for the separation of vanadium from other cations.

(3) Accordingly, space velocity is 9.

(4) At a pH corresponding to the intermediate color of methyl orange, quinquevalent vanadium reacts with 8-hydroxyquinoline to give a compound soluble in chloroform with a Bordeaux red to black color. This sensitive and persistent color of the vanadium-8-hydroxyquinoline salt in chloroform layer can be used for the most sensitive and accurate colorimetric determination of this element.

Experiment II. Quinivalent Vanadium Ion Exchange in C^{NaNa} .

Using C^{NaNa} , nearly the same process⁽⁵⁾ as in Expt. 1 was carried out. The results are shown in Table 2.

Table 2.

Experiment number		7	8	9	10	11	12
Sample solution	pH	12.4	12.1	5.4	5.4	5.0	1.3
	Amount of V $\left\{ \begin{array}{l} r/c.c. \\ \text{Total amount } (r) \end{array} \right.$	6.0	6.0	1.0	6.0	6.0	1.0
		60.0	60.0	60.0	60.0	60.0	60.0
	Total volume (c.c.)	10.0	10.0	60.9	10.0	10.0	60.0
Amount of washings (c.c.)		50.0	50.0	50.0	50.0	50.0	50.0
V, found in effluent (r)		59.6	59.4	60.1	60.0	60.2	17.5
Error	r	-0.4	-0.6	+0.1	0.0	+0.2	-42.5
	%	-0.6	-1.0	+0.2	0.0	+0.3	-70.8

In Expts. 7, 8, 9, 10 and 11, where pH 5.0 or more is used, vanadium passes through C^{NaNa} within experimental error, while in Expt. 12, namely in case of pH 3, only a little part of vanadium is detected in the effluent.

Experiment III. Quinivalent Vanadium Ion Exchange in C^{NaH} .

Using C^{NaH} , much the same process⁽⁶⁾ as in Expt. 1 was carried out. The results are shown in Table 3.

Table 3.

Experiment number		13	14	15	16	17	18	19	20	21
Sample solution	pH	10.0	8.0	5.4	5.0	3.0	3.0	2.2	2.2	1.8
	Amount $\left\{ \begin{array}{l} r/c.c. \\ \text{of V } \left\{ \begin{array}{l} \text{Total amount } (r) \end{array} \right. \end{array} \right.$	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
		36.0	48.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0
	Total volume (c.c.)	15.0	20.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Amount of washings (c.c.)		50.0	50.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0
V, found in effluent (r)		36.4	-8.5	24.0	24.0	21.3	20.4	16.9	16.5	7.0
Error	r	-0.4	-0.5	0.0	0.0	-2.7	-3.6	-7.1	-7.5	-17.0
	%	-1.1	-1.0	0.0	0.0	-11.3	-15.0	-29.6	-31.3	-70.9
V found in effluent V in sample solution $\times 100$		101.1	101.0	100.0	100.0	88.7	85.0	70.4	68.7	29.1

In Expts. 13, 14, 15 and 16, namely where pH 5.0 or more is used, vanadium passes through C^{NaH} within the experimental error. And, in

(5) Ammonium hydroxide was not added before concentrating the effluent.

(6) The pH of sample solutions were adjusted with ammonium hydroxide and nitric acid. Ammonium hydroxide was not added before concentrating the effluent.

Expts. 17–21, namely pH 3 (Expts. 17 and 18), pH 2.2 (Expts. 19 and 20) and pH 1.8 (Expt. 21), the lower the pH of the sample solutions, the larger the amount of vanadium captured by C^{NaH} becomes.

Experiment IV. Quinivalent Vanadium Ion Exchange in C^{NH_4H} .

In Expts. I, II and III, the outline of the quinivalent vanadium ion exchange in the column of cation-exchange resin is shown, so, in the next experiments the more detailed study has been carried out through C^{NH_4H} , which is very convenient for various practical and theoretical purposes.

Table 4.

Experiment number		22	23	24	25	26	27	28	29	30
Sample solution	pH	7.6	7.2	6.4	6.4	5.0	5.0	4.7	4.2	3.8
	Amount of V	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
	$\left\{ \begin{array}{l} r/\text{c.c.} \\ \text{Total} \\ \text{amount}(r) \end{array} \right.$	26.1	52.2	13.1	13.1	13.1	26.1	26.1	23.1	26.1
	Total volume (c.c.)	10.0	20.0	5.0	5.0	5.0	10.0	10.0	10.0	10.0
Amount of washings(c.c.)		60.0	60.0	30.0	30.0	30.0	60.0	60.0	60.0	60.0
ϵ of effluent		0.466	0.905	0.264	0.258	0.260	0.412	0.460	0.405	0.169
V, found in effluent (r)		26.0	51.9	13.2	13.0	13.1	26.2	25.6	22.1	8.0
ϵ_0 (Theoretical value)		0.469	0.911	0.261	0.261	0.261	0.469	0.461	0.469	0.160
Error	$\epsilon - \epsilon_0$	-0.003	-0.006	-0.003	-0.003	-0.001	-0.003	-0.009	-0.064	-0.300
	r	-0.1	-0.3	-0.1	-0.1	0	-0.1	-0.5	-4.0	-18.1
	%	-0.4	-0.6	-0.8	-0.8	0	-0.4	-1.9	-15.3	-69.3
$\frac{\text{V found in effluent}}{\text{V in sample solution}} \times 100$		99.6	99.4	100.8	99.2	100.0	100.4	98.1	84.7	30.7

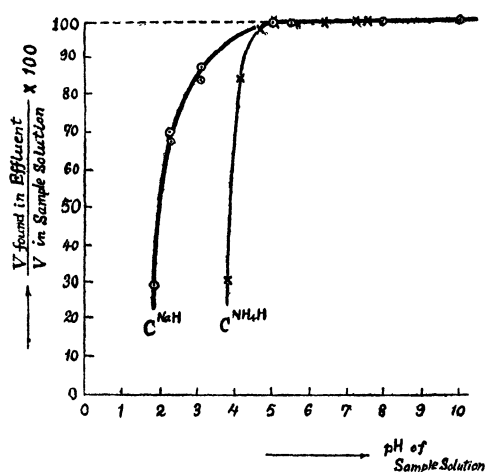


Fig. 2.

After passing vanadium solution (in this case pH was adjusted with ammonium hydroxide and sulfuric acid) through C^{NH_4H} and washing with 30–60 c.c. of distilled water, effluent was gathered in a separating funnel and neutralized with 0.2N sulfuric acid using methyl orange as indicator. Then, vanadium in it was colorimetrically determined by the oxine-chloroform method. The results are shown in Table 4.

In Expts. 22, 23, 24, 25, 26 and 27, namely, where pH 5.0 or

more is used, vanadium exactly passes through C^{NH_4H} . However, as pH decreases, the amount of vanadium captured by C^{NH_4H} increases just as in Expt. III.

In Fig. 2, the relation between the vanadium found in effluents and pH of sample solutions is illustrated in the case of C^{NaH} and C^{NH_4H} .

Conclusion.

Quinquevalent vanadium in aqueous solution is thoroughly captured by C^{HH} independently of pH of passing solutions. It passes, however, quantitatively through C^{NaNH_4} , C^{NaH} or C^{NH_4H} , if the pH of the passing solution is higher than 5.0; but it is partially captured by them, when the pH is lower than 5.0.⁽⁷⁾

The author wishes to thank Dr. Eiiti Minami, Professor of Analytical Chemistry, Tokyo University, and Mr. Masatake Honda, who have given him kind advice and suggestion in this problem.

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The Sunflavor of Beer. II. Essential Substance of Sunflavor.

By Yataro OBATA and Tei YAMANISHI.

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As reported in the previous paper⁽¹⁾ we have ascertained that the essential substance of sunflavor of beer is thioglycolic acid ethylester, and we could also prove chemically and biologically that the essential substance was produced from dithiodiglycolic acid diethylester (-S-S-) which originated in cystine within malt juice by the reducing function of certain unknown components in beer under exposure to sunlight.

It has already been recognized that the malt of the raw material of beer contains the ferments belonging to dehydrase⁽²⁾ and flavine⁽³⁾ and that the solution of autolysed beer-yeast also contains a large amount of dehydrase⁽⁴⁾ and flavin⁽⁵⁾. So we can easily expect that at least these

(1) Y. Obata and T. Yamanishi, *Agriculture*, (Japan) **9** (1947), 537.

(2) A. Foder and L. Frankenthal, *Biochem. Z.*, **225** (1930), 417.

(3) P. Karer and K. Schöpp, *Helv. Chem. Acta.*, **17** (1934), 1013.

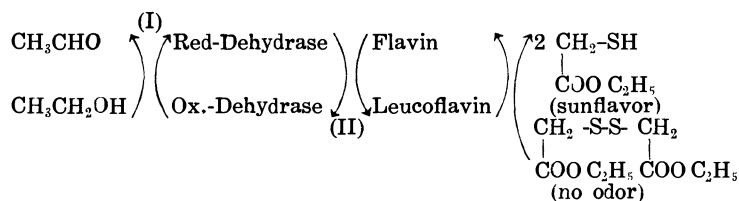
(4) H. v. Euler and H. Adler, *Z. prakt. Chem.*, **235** (1935), 122.

(5) O. Warburg and W. Christian, *Biochem. Z.*, **266** (1933), 377.

ferments in beer yeast will be excreted into beer while its fermentation proceeds.

In fact it is reported that beer contains about 0.26 mg. of flavin per liter⁽⁶⁾, and we could prove the existence of dehydrase in un-Pasteurized beer by the fact that such beer discolored methylene blue solution.

As we could presume that the flavin and dehydrase would take part in the development of the sunflavor of beer, we carried out an experimental study on the mechanism of sunflavor production with dehydrase prepared from beer yeast as well as with flavin. The result was just as we had presumed. Namely, we could prove that by the joint function of these two factors -S-S- was reduced and consequently sun-flavor was produced. This mechanism can be shown with chemical formula as follows:



The change of flavin to leucoflavin by dehydrase is accelerated by sunbeam.

Experimental Part.

Preparation of dehydrase solution. (i) Preparation of dehydrase acetone-sample. Concentrated suspension of beer-yeast which was previously washed twice with water, is cooled with ice, to which is added cold acetone gradually while stirring vigorously. By this treatment the cell membranes of beer-yeast are broken, and the suspension becomes voluminous.

Then it is rapidly filtered by suction, washed twice with acetone and finally washed once more with ether. By drying the residue in vacuum desiccator for one day white powder is obtained.

(ii) Preparation of dehydrase solution. 5 g. of dehydrase-acetone sample thus prepared is suspended in 100 c.c. of K_3PO_4 solution (pH 7.2) and kept in the thermostat at 28°C for two hours. When it is filtered, a clear pale yellow colored solution is obtained.

Experiment on the sunflavor production. (1) By dissolving K_3PO_4 in 3% alcohol, the latter is made to have pH 7.2 (optimum pH of alcohol-dehydrase). Two colorless glass vessels with a glass-stopper containing 10 c.c. are filed with the solution composed of 8 c.c. of the above mentioned alcohol, 2 c.c. of dehydrase solution and 1 mg. of flavin (Sankyo's injection drug).

(6) S. Komatsu et. al., *Chem. and Eng.*, (Japan) **41** (1938), 158.

One bottle is kept in darkness and the other is exposed to sunlight.

After 90 min., the content of the former shows no change, while that of the latter becomes completely colorless and tells the change of flavin to leuco-flavin.

If one drop of -S-S- is sunk in this colorless liquid, the yellowish color comes back around -S-S-.

This means flavin is changed to the oxidized form. Accompanied with this change sunflavor is clearly produced.

If the solution used in this experiment lacks 3% alcohol or keeps its acidity at pH 5.4, its discoloration after 90 min. exposure to sunlight will be very faint.

Thus it can be concluded that in the reaction-system under consideration alcohol is necessary as its substrate and the optimum pH is at 7.2. These conditions coincide with those concluded in the previous report of one study connected with the sunflavor production by beer-yeast.

(2) On examining if dehydrase or flavin added separately can generate the sunflavor, it was concluded that their joint addition was necessary to induce the phenomenon in question as shown in Table 1.

Table 1.

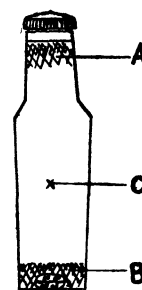
Condition	Reaction system and sunflavor production	
Exposed in sunlight	-S-S- (-)	-S-S-+D (±)
„	-S-S-+F (±)	-S-S-+D+F(*) (+)
Kept in darkness	-S-S-+F (-)	-S-S-+D+F (-)

(+) and (-) denote respectively that sunflavor is generated or not generated after 90 min. -S-S- denotes the substrate solution of the reaction which is at pH 7.2 being composed of 100 c.c. of the saturated solution of dithiodiglycolic acid diethylester, 3 c.c. of alcohol and 2.5 gr. of K_3PO_4 . F denotes 2 mg. flavin (injection drug) dissolved in 20 c.c. of K_3PO_4 solution (pH 7.2). D denotes dehydrase solution prepared from beer yeast as in the experiment (1).

These three kinds of solution are mixed in the following proportion. One c.c. each of D and F are taken and poured together in the glass vessel explained in the experiment (1).

Then the remaining space of the vessel is filled up with -S-S-.

As the vessel is thus filled up with reaction solution perfectly, the experiment is carried out under an anaerobic condition.



A : Yellow,
oxidation by air.
B : Yellow,
oxidation by -S-S-.
C : Colorless.

(3) Test on the presence of dehydrase in beer and destruction of dehydrase by heating.

The glass vessel explained above was filled with 8 c.c. of un-Pasteurized beer and 2 c.c. of $1/25000$ methylene blue solution, and kept at room temperature.

Even after 3 days the color of the solution showed little change.

To accelerate the reaction pH of un-Pasteurized beer was raised from its natural value 4.2 to the optimum for the function of dehydrase or 7.2 and the vessel was placed in the thermostat regulated at 22°C. The color of the solution then faded perfectly after 2 days.

Un-Pasteurized beer comes very quickly to give off sunflavor while Pasteurized beer does so very slowly. This fact suggests that the dehydrase becomes functionless by heating. Pasteurized beer, which had previously been heated at 60°C for 30 min., was examined by the methylene blue test under the same condition as the preceding experiment. The solution was unchanged in color even after 3 days.

This proves the perfect loss of the dehydrase function in Pasteurized beer.

On the other hand, if the reaction-system ^(*) in the experiment (2) had previous been heated at 60°C for 30 min., methylene blue was not reduced and sunflavor was not given off by exposing the solution to sunlight.

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Inhibitory Effect of Cyanine- and Styryl-Dyes upon Cholinesterase. I.

By Eiji HASE, Yoshihisa MIZUNO and Masujiro KATAYANAGI.

(Received June 13, 1949.)

During the past several years it has repeatedly been reported that certain cyanine- and styryl-dyes, usually known as photosensitizers,⁽¹⁾ have some therapeutic effect against certain kind of diseases.⁽²⁾ The mechanism

(1) T. Ogata, "Photosensitive Dyes" ("Kankō-shikiso" in Japanese), Sankaidō-shoten, Tokyo, 1941.

(2) A. D. Welch, L. Peters, E. Beuding, A. Valk and A. Higashi, *Science*, **105** (1947), 486; L. G. S. Brooker and L. A. Swett, *Science*, **105** (1947), 496.

of this chemotherapeutic action remains as yet wholly unknown. Not only from the pharmacological point of view, but also from the purely enzymological view-point, it may be worth while to investigate the action of these substances which have the peculiar physico-chemical properties upon the activities of different enzymes.

Brooker and Swett⁽²⁾ have reported that cyanine- and styryl-dyes have no appreciable effect upon various oxidative enzymes studied. On the other hand, Hino and his coworkers⁽³⁾ have shown that some of these dyes exhibit strong inhibiting action upon catalase. In the present study, it is shown that certain substances belonging to the same category exert remarkable suppressing effect upon the activity of cholinesterase. Whether this effect has anything to do with the chemotherapeutic action reported or not is the problem to be worked out in the future.

Experimental Method.

The activity of cholinesterase was measured by the potentiometric titration method after Alles and Hawes⁽⁴⁾ with a slight modification for our experimental purpose. The dyes were dissolved in one per cent ethyl alcohol solution.* The mixture of enzyme and dye was regulated to pH 7.5 and left in a thermostat at 30°C for 10 min. After the addition of the substrate, the acid liberated by hydrolysis of ester was constantly neutralized with 0.04 N NaOH and its volume consumed was recorded against time. The estimation of the reaction rate was made on the initial part of the alkali-time curve thus obtained. The concentration of the substrate used was sufficiently high so that the rate of hydrolysis remained practically constant during the course of the experiment (10 min.).

Results.

Inhibition of the cholinesterase activity in horse serum by certain cyanine- and styryl-dyes. The inhibitory effects of about one hundred of cyanine- and styryl-dyes were examined. It was found that almost all of them show more or less strong inhibitory action upon cholinesterase activity in horse serum. Several examples of these dyes which exhibit most strong inhibitory effects are shown in Table 1. Their efficacies are compared in terms of concentration causing 50 per cent inhibition with those of substances which have thus far been known as strong inhibitors of cholinesterase.

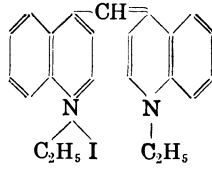
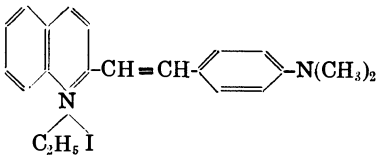
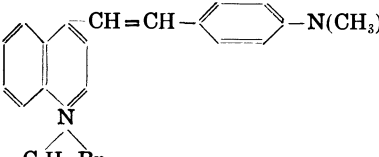
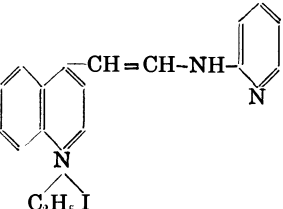
It may be seen that the action of dyes is by far stronger than most of the substance listed, although it is less than one hundredth of the activity of eserine.

(3) S. Hino, Y. Ogura, M. Fujita and K. Shibata, Unpublished paper read before the Chem. Soc. Jap. in 1948.

(4) G. A. Alles and R. C. Hawes, *J. Biol. Chem.*, **133** (1940), 377.

* It was ascertained that ethyl alcohol had no effect upon cholinesterase under these experimental conditions.

Table 1.
Inhibitory effects of some cyanine- and styryl-dyes
upon cholinesterase in horse serum.

	Inhibitor	Concentration of the inhibitor causing 50% inhibition (mol/l.).
Cyanine-dyes	 1, 1'-Diethyl-4, 4'-monomethine-quinocyanine iodide	$10^{-5.4}$
	$C_{30}H_{39}S_2N_2I$	$10^{-5.5}$
Styryl-dyes	 <i>p</i>-Dimethylamino-benzyliden-quinaldine ethiodide	$10^{-5.6}$
	 <i>p</i>-Dimethylamino-benzyliden-lepidine ethobromide	$10^{-5.4}$
	 4-(α-Pyridylamino)-ethenyl-quinoline ethiodide	$10^{-5.4}$
Other substances	Eserine salicylate	$10^{-7.9}$
	Strychnine sulphate	$10^{-4.6}$
	Quinine hydrochloride	$10^{-4.1}$
	Atropine sulphate	$10^{-2.6}$

All these measurements were carried out under the same experimental conditions; *pH* of the reaction mixture, 7.5; concentration of the substrate (acetylcholine chloride), 0.02 mol/l.; the temperature, 30°C.

Effects upon the "specific" and "non-specific" cholinesterase. Recently it has been found⁽⁵⁾ that there are two types of cholinesterase, the "specific" and the "non-specific". Using one of the most active cyanine dyes found in the previous experiment, the susceptibility of the two different types of cholinesterase was compared. As may be seen in Table 2 the non-specific cholinesterase seems to be more strongly inhibited than the specific one. Since, however, the preparation of the specific cholinesterase used in this experiment was not sufficiently homogeneous, the results obtained do not allow us to conclude definitely and quantitatively the difference in the susceptibilities of the two cholinesterases.

Table 2.

Effects of some cyanine- and styryl-dyes upon various esterases.

Dye	Enzyme	Source of enzyme	Substrate	Concentration of the dye causing 50% inhibition of enzyme activity (mol/l.)
1, 1'-Diethyl-4, 4'-mono-methine-quino-cyanine iodide	Non-specific cholinesterase	Horse serum	Acetylcholine chloride (0.02 mol/l.)*; pH, 7.5; 30°C	$10^{-5.4}$
„	Specific cholinesterase	Homogenate of horse brain	Acetylcholine chloride (0.002 mol/l.)*; pH, 7.5; 30°C	$10^{-4.6} \sim 10^{-4.8}$
„	Esterase	Horse serum	Methylbutyrate and triacetin at various concentrations; pH, 7.5; 30°C	Slight activation
Various cyanine- and styryl-dyes	Esterase	Pig liver extract	Methylbutyrate (0.1 mol/l.); pH, 7.5; 30°C	No measurable effect

* Concentration of substrate applied was nearly saturating for the reaction velocity observed in each case.

Effects upon other esterases. Effects of cyanine- and styryl-dyes upon the esterase in horse serum were examined, methyl butyrate and triacetin being used as the substrate. It was found that some of the dyes examined increase slightly the activity of this enzyme and others have no measurable effects. It was further ascertained that the dyes have no appreciable effects upon the activity of liver esterase (Table 2).

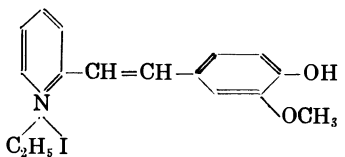
At any rate, it can be concluded that the inhibitory effect of the dyes is quite specific to the cholinesterase, whether "specific" or "non-specific".

(5) A. M. Wynne, *Ann. Rev. Biochem.*, **15** (1946), 63.

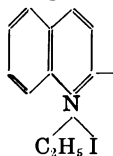
Relationship between the chemical constitution and the inhibitory effect. Comparison of efficacy of structurally related styryl-dyes shows us that there exists certain relationship between structure and inhibitory effect (see Table 3). It can be seen from the table that the dimethylamino radical, attached to benzene ring in the molecule, has the most favorable effect upon the inhibitory action of the dye.

It is another interesting problem that vanillylidenpicolin ethiodide, which contains a pyridine nucleus, has no appreciable effect upon cholinesterase, while vanillylidenquinaldine ethiodide, possessing a quinoline nucleus, exhibits a considerable inhibitory action under the same experimental conditions.

Table 3. Relationship between the chemical constitution of the related styryl-dyes and their inhibitory effects upon the cholinesterase in horse serum.

Chemical structure of dye		Concentration of the dye causing 50% inhibition (mol/l.)**
I	$\phi^* - \text{CH} = \text{CH} - \text{C}_6\text{H}_4 - \text{N}(\text{CH}_3)_2$ <i>p</i> -Dimethylamino-benzyliden-quinaldine ethiodide	$10^{-5.6}$
II	$\phi - \text{CH} = \text{CH} - \text{C}_6\text{H}_4 - \text{OH}$ <i>p</i> -Hydroxybenzyliden-quinaldine ethiodide	$10^{-5.0}$
III	$\phi - \text{CH} = \text{CH} - \text{C}_6\text{H}_3(\text{OH})(\text{OCH}_3)$ Vanillyliden-quinaldine ethiodide	$10^{-4.8}$
IV	$\phi - \text{CH} = \text{CH} - \text{C}_6\text{H}_3(\text{OCH}_2)_2$ Piperonyliden-quinaldine ethiodide	$10^{-4.7}$
V	 Vanillyliden-picoline ethiodide	No appreciable effect even at the concentration of $10^{-4.0}$ mol/l.

* The symbol ϕ represents the quinaldine ethiodide nucleus



** Experimental condition; *p*H, 7.5; temperature, 30°C; concentration of substrate (acetylcholine chloride), 0.02 mol/l.

Summary.

- (1) It was found that a number of cyanine- and styryl-dyes has a strong inhibitory action upon cholinesterase.
- (2) Both the specific and non-specific cholinesterase are inhibited by the substances, the latter being probably more susceptible than the former.
- (3) The substances have no appreciable effects upon the liver esterase. With the esterase in horse serum, even a slight acceleration of the activity was observed under the influence of some dyes investigated.
- (4) For some related members of styryl-dyes, a certain relationship between chemical constitution and their inhibitory effects upon cholinesterase could be found.

We wish to express our sincere gratitude to Professor H. Tamiya and Doctor A. Takamiya for their kind guidance and to Mr. Innami for his assistance in this work. These experiments were largely supported by the Scientific Research Encouragement Grant and the Grant-in-aid for Private Research Institute donated by the Ministry of Education, to which our thanks are due.

The Tokugawa Institute for Biological Research.

**On the Configurations of the Peptide Linkage in Proteins
and Some Other Substances, as Revealed by
Their Near-Infrared Absorption Spectra.**

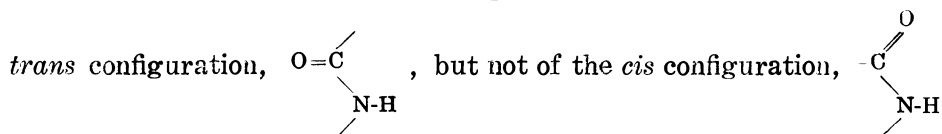
By Masamichi TSUBOI.

(Received June 29, 1949.)

As continuation of his investigation on the hydrogen bondings in compounds with the peptide linkage,⁽¹⁾ the writer made 3μ region infrared absorption measurements of some proteins, diketopiperazine, some amides, some lactams, etc., in the solid or the liquid state. In this paper the writer reports some results of these measurements and gives interpretations of them in the light of the knowledge, previously obtained,

(1) M. Tsuboi, This Bulletin, **22** (1949), 215.

of the 3μ region absorptions of amides in carbon tetrachloride solutions.⁽¹⁾ A conclusion reached is that the peptide linkage in proteins is of the



Experimental.

The infrared monochromator and other apparatus used in the present investigation are the same as those described in the previous paper.⁽¹⁾ The samples examined are:

N-Methylacetamide, $\text{CH}_3\text{CO-NHCH}_3$. Purified by vacuum distillation. Melting point: 28°C .

δ -Valerolactam, $\begin{array}{c} \text{CH}_2\text{-CH}_2\text{-CH}_2 \\ | \\ \text{CH}_2\text{-CO-NH} \\ | \\ \text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2 \end{array}$. Purified by vacuum distillation. Melting point: 40°C .

ϵ -Caprolactam, $\begin{array}{c} \text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2 \\ | \\ \text{CH}_2\text{-CO-NH} \end{array}$. Supplied by K. Hoshino and H. Yumoto. Purified by vacuum distillation. Melting point: 68°C .

Formamide, HCONH_2 . Purified by vacuum distillation.

Diketopiperazine, $\begin{array}{c} \text{NH-CH}_2\text{-CO} \\ | \\ \text{CO-CH}_2\text{-NH} \end{array}$. Prepared by A. Mukai. Purified by repeated recrystallization from hydrochloric acid using methanol.

Poly- ϵ -capramide ("Amilan").⁽²⁾ $\dots(\text{CH}_2)_5\text{CONH}(\text{CH}_2)_5\text{CONH}\dots$. Supplied by K. Hoshino and H. Yumoto. Dried over calcium chloride.

Egg albumin. Prepared according to the method of Kekwick, and purified by recrystallization by H. Sugano. A suitable film for the infrared absorption measurements was obtained by spreading a drop of aqueous solution of egg albumin on a cover glass (the salt contained being removed by dialysis), and drying it first over calcium chloride and then over phosphorus pentoxide.

Horse serum albumin. Prepared according to the method of Kekwick, and purified by recrystallization by S. Nakamura. A film of this protein was prepared in the same way as that of egg albumin.

Results and Interpretations.

The results obtained are shown in Fig. 1, where $\log I_0/I$ is plotted against wave-length, I_0/I being the ratio of the intensity of light transmitted by blank space to that by the film.

Before proceeding to the interpretation of these results, the assignments of N-H absorption bands of compounds with the peptide linkage, described in detail in the previous paper,⁽¹⁾ may be summarized in Table 1. These relations were obtained by studying the effects of the concentrations and the temperatures of carbon tetrachloride solutions of N-methylacetamide and several other amides and δ -valerolactam on the 3μ region absorption spectra. Compounds with the peptide linkage show the strong tendency of forming intermolecular and intramolecular N-H...O=C bondings; accordingly most of N-H's and C=O's in these compounds

(2) Material of synthetic fibers, made by Tōyō Rayon Co.

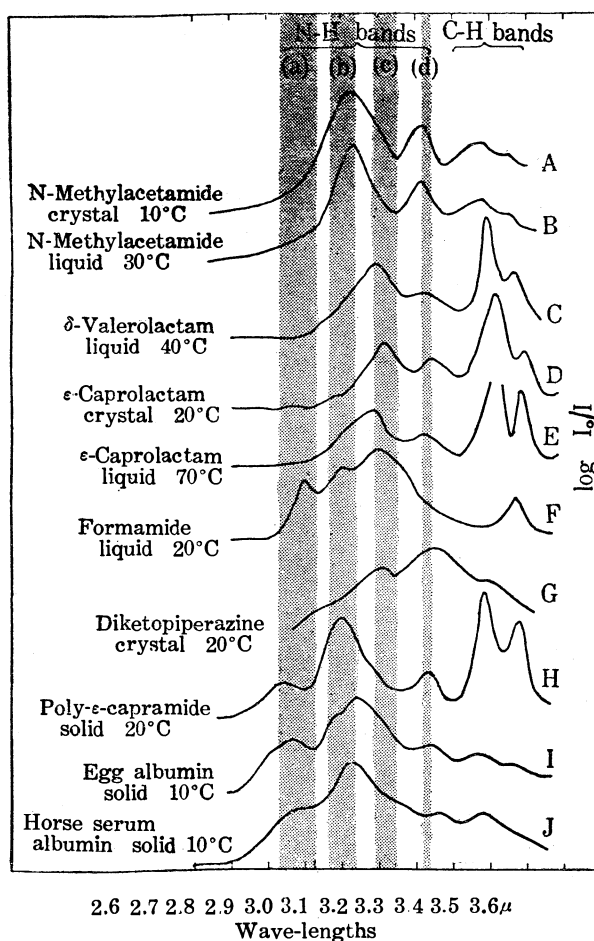


Fig. 1. 3μ region infrared absorption curves of some compounds with peptide linkage.

must form hydrogen bondings in the liquid and the solid states. On the

other hand, as is shown in Table 1, N-H in $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{N} - \text{H} \end{array}$ gives an associa-

tion band in $2.97 \sim 3.04\mu$ region, and N-H in $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{N} - \text{H} \end{array}$ an association band in $3.09 \sim 3.15\mu$ region.* Hence, we can tell whether the peptide linkage is of the trans configuration or of the cis configuration, according as the N-H association band appears in the $2.97 \sim 3.04\mu$ region or the $3.09 \sim 3.15\mu$ region. Using this relation, the configurations of CONH

* This difference in wave-lengths of N-H association bands is attributable to the difference in the positions of H relative to other atoms, as detailed in the author's previous paper.⁽¹⁾

Table 1.
The assignments of N-H bands of compounds
with the peptide linkage.

Wave-lengths (in μ) of absorption maxima	Assignments
(a) 2.83~2.93	Free N-H
(b) 2.97~3.04	$\begin{array}{c} \text{...O=C} \diagup \text{N-H...O=C} \diagup \text{N-H...} \\ \text{N-H in} \end{array}$ $\text{or ...O=C} \diagup \text{N-H...O=C} \diagup \text{N-H...},$ where H on N is <i>trans</i> to O.
(c) 3.09~3.15	$\text{N-H in } \begin{array}{c} \text{O...H-N} \diagdown \text{C-} \\ \text{N-H...O} \diagup \end{array} \text{ or } \begin{array}{c} \text{O...H-N} \diagdown \text{C-} \\ \text{N-H...O=C} \end{array}$ where H on N is <i>cis</i> to O.
(d) 3.22~3.24	Not uniquely assigned. The band may be assigned to something that accompanies the formation of intermolecular hydrogen bonding N-H...O. In the molecules here concerned H on N may be either <i>trans</i> or <i>cis</i> to O.

may be determined as shown in Table 2, and the absorption curves in Fig. 1 may be interpreted as follows:

N-Methylacetamide. (Cf. Fig. 1, A and B.) N-Methylacetamide, in the crystalline state, shows the absorption maxima at 3.03μ and 3.22μ , but not at $3.09\sim 3.15\mu$. This shows that the crystal consists only of *trans* molecules (molecules in each of which H on N is *trans* to O), and

Table 2.
Configurations of CONH, determined from the wave-lengths
of absorption maxima of N-H...O bands.

Samples		Wave-lengths (in μ) of absorption maxima of N-H...O bands		Configurations of CONH
N-Methylacetamide	(crystal)	3.03	3.22	<i>trans</i>
"	(liquid)	3.03	3.22	<i>trans</i>
δ -Valerolactam	(liquid)	3.09	3.23	<i>cis</i>
ϵ -Caprolactam	(crystal)	3.11	3.24	<i>cis</i>
"	(liquid)	3.09	3.23	<i>cis</i>
Formamide	(liquid)	3.00	3.10	<i>trans</i> and <i>cis</i>
Diketopiperazine	(crystal)	3.11	3.26	<i>cis</i>
Poly- ϵ capramide	(solid)	3.00	3.23	<i>trans</i>
Egg albumin	(solid)	3.04	3.24	<i>trans</i>
Horse serum albumin	(solid)	3.03	2.25	<i>trans</i>

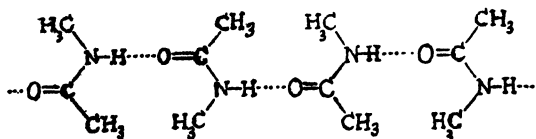


Fig. 2.

has a structure such as shown in Fig. 2. It is interesting to note that, according to C. J. Brown and D. E. Corbridge,⁽³⁾ acetanilide has the crystal structure (hence the molecular structure) as shown in Fig. 3, which is of the same type as that of N-methylacetamide shown in Fig. 2.

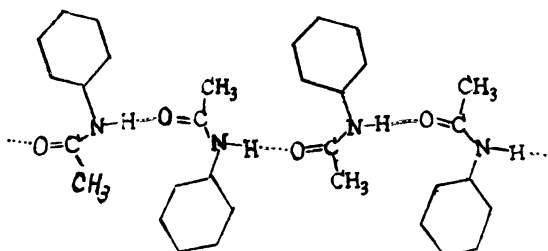


Fig. 3. After C. J. Brown and D. E. Corbridge.

N-Methylacetamide, in the liquid state, also shows the absorption maxima at 3.03μ and 3.22μ with nearly the same intensities (relative to those of the C-H bands) and widths of the bands as in the crystalline state. This shows that the molecule of N-methylacetamide is linked in nearly the same manner in the liquid state as in the crystalline state, at least at the temperatures a little above its melting point.

δ -Valerolactam. (Cf. Fig. 1, C.) δ -Valerolactam, in the liquid state, shows absorption maxima at 3.09μ and 3.23μ , i. e. at wave-lengths, respectively, shorter than 3.11μ and 3.24μ , which are the wave-lengths of absorption maxima of δ -valerolactam in carbon tetrachloride solution.⁽¹⁾ This fact may be explained as due to some structural deformation of the ring dimers (to which the 3.11μ and 3.24μ bands were assigned⁽¹⁾), caused by closer mutual approach of the molecules of δ -valerolactam.

ϵ -Caprolactam. (Cf. Fig. 1, D and E.) ϵ -Caprolactam, in the crystalline state, shows absorption maxima at 3.11μ and 3.24μ , but not at $2.97\sim 3.04\mu$. This shows that in ϵ -caprolactam molecules in the crystalline state, H on N is *cis* to O.

ϵ -Caprolactam, in the liquid state, shows two N-H association bands whose maxima lie at 3.09μ and at 3.23μ ; hence, in this molecule H on N is *cis* to O, also in the liquid state, although these two bands are shorter in wave-lengths, weaker in absorption intensities (relative to those of the C-H bands), and broader than the 3.11μ and 3.24μ bands of ϵ -caprolactam in the crystalline state.

(3) C. J. Brown and D. E. Corbridge, *Nature*, **162** (1948), 72.

Formamide. (Cf. Fig. 1, F.) Formamide, in the liquid state, gives N-H association bands at 3.00μ and 3.10μ . They may be assigned to the stretching vibrations of N-H's, the 3.00μ band to that in which H on N is *trans* to O, and the 3.10μ band to that in which H on N is *cis* to O. Besides, it also gives a band at the free N-H region. This reveals that N-H's of formamide are partially in free state even in its pure liquid state—an unusual phenomenon for an associated liquid.

Diketopiperazine. (Cf. Fig. 1, G.) Diketopiperazine, in crystalline state, shows N-H bands at $3.11\mu^{(4)}$ and 3.26μ , but not at $2.97\sim 3.04\mu$, revealing that the CONH of this substance is of the *cis* configuration. This is in agreement with the experimental results of X-ray analysis by Go and Ohashi⁽⁵⁾ and by Corey⁽⁶⁾ (see Fig. 4).

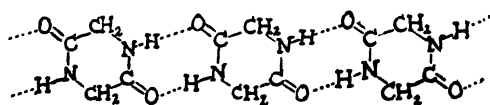
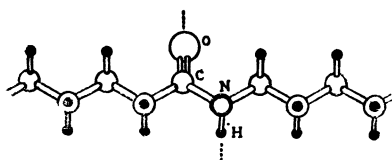
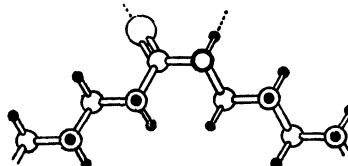


Fig. 4. After R. B. Corey

Poly- ϵ -capramide. (Cf. Fig. 1, H.) There are absorption maxima for poly- ϵ -capramide at 3.00μ and at 3.23μ , but none in the $3.09\sim 3.15\mu$ region.⁽⁷⁾ This shows that H on N in poly- ϵ -capramide is *trans* to O. It follows then that the chain $\dots\text{--CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{--}\dots$ in this substance must be of the form as shown in Fig. 5 (A), but not of the form as shown in Fig. 5 (B).



(A) H on N is *trans* to O.



(B) H on N is *cis* to O.

Fig. 5.

Proteins. (Cf. Fig. 1, I and J.) The molecules of proteins have as their constituents various atomic groups that give absorption bands in the 3μ region. They are shown in Table 3, with the wave-lengths of

(4) The 3μ region absorption curve of solid film of diketopiperazine has already been obtained by A. M. Buswell and others in 1940 (*J. Am. Chem. Soc.*, **62** (1940), 2759). They observed an absorption at 3.14μ , but they suspected this to be due to glycine, which might be produced as a dissociation product in the preparation of the film. The present writer observed an absorption at 3.11μ (probably corresponding to that at 3.14μ observed by Buswell) even in a film confirmed to be free from glycine by the K. Kuratani's infrared absorption measurements in the rock salt region.

(5) Go and Ohashi, Paper communicated to Chem. Soc. Japan, at its 60th Annual Meeting, April 1938.

(6) R. B. Corey, *J. Am. Chem. Soc.*, **60** (1938), 1598.

(7) See foot-note (9).

Table 3.

Atomic groups	Wave-lengths (in μ) of absorption maxima	Number of the groups in one molecule	
		Egg albumin	Bovine serum albumin
>C-H	3.35~3.60	2050	3390
$\text{>C-H}^{(a)}$	3.21~3.30	150	270
CONH	2.97~3.26 (2.83~2.93 in free state)	430	690
$\text{N}^+\text{-H}$	3.14~3.28	} 80	180
$\text{N-H}^{(b)}$	2.83~2.95		
$\text{COOH}^{(c)}$	3.27~3.89 (2.79~2.84 in free state)	$\leq 50^{(c)}$	$\leq 90^{(c)}$
OH	2.83~3.22 (2.75~2.77 in free state)	50	80

(a) C-H with unsaturated C.

(b) Amino group may be mostly of $\text{N}^+\text{-H}$ form, that of N-H form being negligible.

(c) Carboxyl group may be mostly of COO^- form, that of COOH form being negligible.

the absorption maxima and the number of each of the atomic groups in one molecule of egg albumin and of bovine serum albumin, estimated from the results of amino acid analyses of these proteins.⁽⁸⁾ As shown in the table, CONH is the most abundant of the atomic groups that give absorption maxima in the 2.97~3.26 μ region. It is this group that determines the essential forms of the absorption curves of these proteins in the said region. Other groups, such as $\text{N}^+\text{-H}$ and O-H , being far less in number, their effects upon the forms of the curves must be very little. The group >C-H , on the other hand, is comparatively large in number, attaining as many as one third of the number of CONH; but since >C-H bands are generally much weaker than N-H association bands in absorption intensities (per one group), its effect is considered to be also negligible. The absorption maxima in the same region of egg albumin and horse serum albumin are at 3.04 μ or 3.03 μ and at 3.24 μ or 3.25 μ ,⁽⁹⁾ but not in the vicinity of 3.11 μ , unlike δ -valerolactam, ϵ -caprolactam, and diketopiperazine, all of which show the absorption maximum near 3.11 μ . Other proteins, according to Buswell and others,⁽¹⁰⁾ also show the absorption maxima at nearly the same positions, except salmin.⁽¹¹⁾

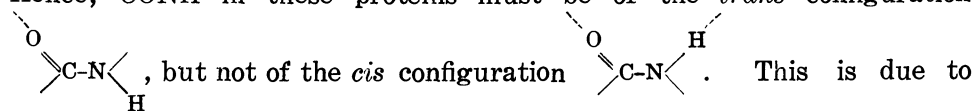
(8) Block, *Advances in Protein Chemistry*, **2** (1945), 119; Stein and Moore, *J. Biol. Chem.*, **178** (1949), 79.

(9) In the last three curves of Fig. 1, besides the absorption maxima mentioned above, there are weak ones at 2.85~2.88 μ , which may probably be attributed to the bound water.

(10) A. M. Buswell, K. F. Krebs and W. H. Rodebush, *J. Phys. Chem.*, **44** (1940), 1126.

(11) The 3.09 μ band of salmin may be due to the N-H 's in guanidinium groups, as Buswell and others indicated in their paper cited in (10).

Hence, CONH in these proteins must be of the *trans* configuration



the molecular structure of proteins, which has been much debated. On this basis any structural view involving the assumption of the *cis* configuration in the peptide linkage is excluded, such as the view assuming the diketopiperazine structure, or the ring dimer structure,

$\begin{array}{c} \text{O} \quad \text{H} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{O} \end{array}$ (10), etc. On the other hand, the structural model of protein molecule recently proposed by Simanouti and Mizushima⁽¹²⁾ is incidentally in accord with the writer's conclusion given above, for in their model the peptide linkage is always and exclusively of *trans* configuration.

The writer wishes to express his sincere thanks to Professor San-ichiro Mizushima and Assistant Professor Takehiko Simanouti for their kind guidance throughout this work.

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(12) T. Simanouti and S. Mizushima, *Kwagaku*, **17** (1947), 24, 52; This Bulletin, **21** (1948), 1.

Studies on Sinomenine. LXI.
On (+)-*epi*-Dihydro-thebainone.

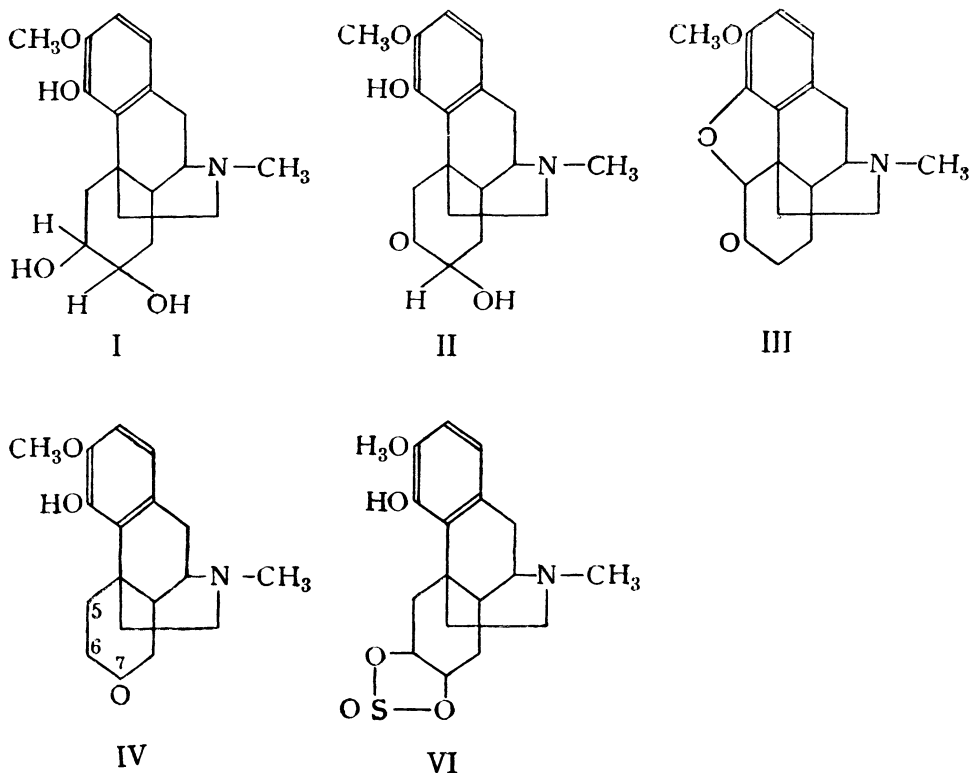
By Kakuji GOTO and Kimiyo MICHII.

(Received July 6, 1949.)

In a previous communication,⁽¹⁾ we reported the formation of (+)-dihydro-codeinone (III) from (+)-dihydro-sinomeninone (II) by boiling the latter in 50% sulfuric acid solution. We applied the same treatment to tetrahydro-sinomeninone (I) to see whether the base is thereby led to the formation of the oxide ring or not. We found, however, that no trace of alkali-insoluble base was formed in this case, but tetrahydro-sinomeninone was transformed into a base (IV) isomeric with the well-known dihydro-

(1) Part LX, *Acta phytochimica*, XV, 187 (1949).

thebainone. The transformation is brought about undoubtedly by a kind of semi-pinacolone rearrangement.



V ($C_7 = \text{CHOH}$)

The formation of (+)-dihydro-codeinone (III) from α -dihydro-sinomeninone (II) necessitates the migration of the hydroxyl groups from C (7) to C (5) around the ketonic group at C (6). This may be effected by anionotropy through the interchange of the positions between the hydroxyl group and the double linking, formed by the enolization of the ketone. The fact that tetrahydro-sinomeninone was not led to the oxide ring closure by the same treatment seems to verify the above supposition to some degree.

The new base, epi-dihydrothebainene, having the molecular formula $C_{18}H_{28}O_3N$ and being soluble in caustic alkali, gives a ferric chloride reaction and forms a monosemicarbazone. It is reduced catalytically into an alcoholic base, epi-dihydrothebainol, and shows properties quite different from dihydrothebainol. Its dibenzoyl derivative crystallizes as methiodide.

In the following table, the properties of the two pairs of the ketonic and alcoholic bases are compared.

	M. p. of free base	$[\alpha]_D$	M. p. of Semicarbazone	M. p. of Methiodide
(+)-Epidihydrothebainone	130°	+37.3°	205°	253°
(+)-Dihydrothebainone ⁽²⁾	152°	+59.17°	235°	122°
(+)-Epidihydrothebainol	154°	+48.6°	—	232°
(+)-Dihydrothebainol ⁽³⁾	165°	+31.5°	—	278°

By the way, we tried the dehydrating action of thionyl chloride on tetrahydrosinomeninone. However, the dehydration did not occur and thionyl chloride formed a cyclic sulfurous acid ester (VI) with the vicinal glycol of the base. This fact coincides well with the investigation of Kitasato and Sone.⁽⁴⁾

The thionyl ester gives the sodium nitro-prusside reaction and regenerates the original base, when warmed with hydrochloric acid, and gives a ferric chloride reaction, thus the phenol group seems to remain intact in the product.

Experimental (By K. M.)

(+)-Epi-dihydro-thebainone (IV). Solution of (+)-tetrahydro-sinomeninone (2 g.) in 55% sulfuric acid (15 c.c.) was boiled for 1.5 hours in an oil-bath. As the concentration of sulfuric acid plays a considerable part on the yield, it should be kept exactly 55%. The cooled solution was diluted with water, made alkaline with caustic and fixed soda, and extracted with chloroform. The chloroform residue was dissolved in acetone and the acetone solution was diluted with ether of its half volume. The precipitate was filtered off and the filtrate was concentrated, dissolved in acetone and rubbed with a glass-rod. The crude base thus crystallized out melted at 120°C. (Yield 0.5 g.). The pure epidihydrothebainone was obtained through its semicarbazone.

Semicarbazone. To the aqueous solution of the above crude base (4 g.), a sufficient quantity of semicarbazide hydrochloride and sodium acetate was added and the mixture was heated for 15 min. on a steam-bath and left overnight. The semicarbazone was isolated with chloroform and recrystallized from alcohol and acetone. M. p. 205°C. Yield 1.6 g. (Found: C, 63.70; H, 7.02; N, 15.79%. Calc. for $C_{19}H_{26}N_4O_3$: C, 63.69; H, 7.26; N, 15.64%.)

Regeneration of the free epi-dihydro-thebainone was effected by boiling the semicarbazone (0.8 g.) with 40% sulfuric acid (20 c.c.) in an oil-bath (130–135°C) for an hour. The free base crystallized out in prisms from acetone. M. p. 130°C. $[\alpha]_D^{10} = +37.3^\circ$ (c=2.200 in chloroform). (Found: C, 72.00; H, 7.455; N, 4.595%. Calc. for $C_{18}H_{23}O_3N$: C, 71.76; H, 7.64, N, 4.65%.)

Methiodide. M. p. 253°C from alcohol. (Found: I, 28.59%. Calc. for $C_{18}H_{23}O_3N$. ICH_3 : I, 28.70%.)

(+)-Epidihydro-thebainol (V). The (+)-epidihydro-thebainone (0.5 g.) was dissolved in methanol (20 c.c.), added with PtO_2 (0.05 g.) and reduced catalytically at 30°C. The

(2) K. Goto and S. Mitsui, This Bulletin, 5 (1930), 282.

(3) Prepared by catalytic reduction in the same way as is shown in the experimental part. These figures coincide well with those given by Skita and others (Ber., 54 (1921), 1560) on (–)-dihydrothebainone, but somewhat differ from those of (+)-dihydrothebainone, prepared by Na-amalgam reduction.⁽¹⁾ A similar case is known in the catalytic reduction of cholestanone (*cis-trans* isomerism of H and OH).

(4) Ber., 64 (1931), 1142.

absorption of hydrogen amounted to 50 c.c. On evaporating the methanolic filtrate, the free base crystallized out in prisms. M. p. 125°C, after sintering at 115°C. However, the dried specimen for analysis melted at 154°C. $[\alpha]_D^{17} = +48.6^\circ$ ($C=1.768$, chloroform). (Found: C, 71.57; H, 8.345; N, 4.49%. Calc. for $C_{18}H_{25}O_3N$: C, 71.29; H, 8.25; N, 4.62%).

Methiodide. M. p. 282°C from alcohol. (Found: I, 28.88%. Calc. for $C_{18}H_{25}O_3N \cdot ICH_3$: I, 28.54%).

Dibenzoyl-(+)-epidihydro-thebainol-methiodide. (+)-Epidihydro-thebainol (0.1 g.) was dissolved in dry pyridine (1 c.c.) cooled with freezing mixture and added with benzoyl-chloride (0.15 g.). The mixture was left overnight and then decanted into a saturated solution of ammonium carbonate. Two days after, the syrupy precipitate was washed with water and taken up in chloroform. The washed and dried chloroform gave an oily residue when evaporated. The dibenzoyl-derivative was too soluble in organic solvents, such as alcohol and benzene and did not crystallize from ether also. It was, therefore, turned into its methiodide in alcoholic solution. M. p. 273°C recrystallized therefrom. (Found: C, 60.53; H, 5.898; N, 2.14; I, 19.23%. Calc. for $C_{33}H_{36}O_5NI$: C, 60.64; H, 5.51; N, 2.14; I, 19.45%).

Thionyl-ester (VI) of (+) tetrahydro-sinomeninone. Dry (+)-tetrahydro-sinomeninone (1 g.) was dissolved in dry pyridine and the solution was slowly decanted into ice-cooled thionyl chloride (6 g.). After being kept standing two hours, the clear solution was poured on ice, and made alkaline with sodium carbonate. The thionylester was then extracted with chloroform. The dried chloroform was distilled off and the remaining pyridine was removed under diminished pressure. The residue crystallized on addition of methanol. Yield 0.8 g. M. p. 189°C from the same solvent. $[\alpha]_D^{22} = +71.7^\circ$ ($C=0.488$, in chloroform). (Found: C, 57.27; H, 6.44; N, 3.55; CH_3OH , 7.89%. Calc. for $C_{15}H_{23}NO_5S \cdot CH_3OH$: C, 57.43; H, 6.80; N, 3.52; CH_3OH , 8.06%). The methanol free ester melted at 191°C.

As it has been already shown⁽¹⁾ that (—)-tetrahydrosinomeninone can be prepared from (—)-dihydrothebainone through a series of reactions, it is quite reasonable to assume that (—)-epi-dihydrothebainone and (—)-epi-dihydrothebainol can be prepared in the same way as above. This part of work must be postponed in future for the lack of materials.

Our hearty thanks are due to Mr. Tetsuro Kono and Miss Yosiko Sudzuki for the micro-analysis in this work, and also to Ministry of Education for a grant, which partly defrayed the cost of the present work.

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Fundamental Research on Anodic Reaction. II.*
Activation Energy of Anodic Oxygen-producing
Reaction on Some Electrode Materials in
Aqueous Solution of N/10 Sodium Hydroxide.

By Yukio YONEDA.

(Received July 23, 1949.)

Introduction. The activation energy of electrode reaction can be measured without the knowledge of true area of electrode surface, therefore it is important for the determination of the mechanism of the electrode reaction. Activation energy of anodic oxygen-producing reaction in aqueous solution of N/5 H_2SO_4 on platinum was determined by F. P. Bowden⁽¹⁾ to be 13–14 kcal./mole after being corrected by the present author on equilibrium oxygen potential, which will be stated in the present paper. H. P. Stout⁽²⁾ and nearly at the same time René Audubert⁽³⁾ published the values of activation energy in alkaline solution, but the values calculated were 25.3 and 8.3 kcal. respectively, different from each other. These results are tabulated in the section of "Discussions".

The influence of time on the overvoltage of oxygen anode is remarkable, as Hickling and Hill⁽⁴⁾ has stated. Therefore it is important to define the time at which overvoltage is measured. Four different definitions of time are possible as follows:

- (a) The time when the maximum curvature on the built-up curve of potential is obtained.
 - (b) The time when the potential reaches to stationary state.
 - (c) The time when the increase of overvoltage per unit time becomes smaller than a certain value.
 - (d) The fixed time after the closing of electric circuit.
- (a) and (b) have some concrete meaning, but (c) and (d) are conventional methods and have rather obscure meaning.

Recently J. N. Agar⁽⁵⁾ published his consideration on the theoretical standpoint of activation energy, and classified it into two categories, that is, E_I and E_{II} . E_I is calculated from $\left(\frac{\partial \log i}{\partial (1/T)}\right)_\eta$, taking the temperature coefficient of equilibrium potential into consideration, and E_{II} ,

* The first paper, *J. Chem. Soc. Japan*, in press.

(1) F. P. Bowden, *Proc. Roy. Soc. London*, A **126** (1929), 107.

(2) H. P. Stout, *Discussions, Faraday Soc.*, No. 1 (1947), 246.

(3) René Audubert, *ibid.*, 72.

(4) A. Hickling and S. Hill, *ibid.*, 236.

(5) J. N. Agar, *ibid.*, 81.

from $\left(\frac{\partial \log i}{\partial (1/T)}\right)_v$, neglecting the temperature coefficient, where V , η and i mean the electrode potential, overvoltage and the current density respectively. From the definition of activation energy, E , is more precise, but it depends upon the value of η . As E , is equal to $\Delta H^\ddagger - \alpha\eta F$, according to Eyring's notation,⁽⁶⁾ the present author adopts,

$$\Delta H^\ddagger = -2.303 R \left(\frac{\partial \log i}{\partial 1/T}\right)_\eta + \alpha\eta F, \dots\dots\dots(1)$$

as true activation energy which should be independent of η , where F is Faraday constant, α is a constant, and T is absolute temperature.

Experimental Procedures. Anode materials used were platinum, magnetite, or natural graphite. Platinum was brightly polished and its apparent area was 5 sq. cm. Magnetite had been shaped from a large artificial magnetite anode of practical size, and its area was 5 sq. cm. As natural graphite, positive plate of dry cell was used, and its area was 5 sq. cm., too. It consisted of natural graphite sintered with organic binder, and was treated with xylene to extract soluble matter.

Electrolyte was the aqueous solution of N/10 NaOH, which was prepared not to be contaminated with carbonate or chloride. As reference electrode, mercuric oxide electrode with N/10 NaOH solution as electrolyte was employed, therefore liquid potential was always negligible. A fine tip from reference electrode was slightly pressed upon the surface of electrode. Electrolyte was always stirred by and saturated with the stream of oxygen gas.

Two electric circuits, that is, ordinary and oscillographic methods, for measuring overvoltage were prepared. The ordinary one consisted of a potentiometer and a galvanometer. The oscillographic method means that with electromagnetic oscillograph and vacuum tube amplifier. The sensibility of vibrator (Yokogawa D type) is 1 mm./ μ A, and the total sensibility, when combined with amplifier and dipped in damping oil, is 0.5 mm./mv.

The potentials by ordinary method both on platinum, (i)*, and on magnetite and natural graphite, (iii)*, were measured. The electrolytic cell was in a thermostat, but the reference electrode was in room temperature. The potential differences caused by this temperature difference were specially measured afterwards and these amounts were corrected for the overvoltage value. In the case of oscillographic method on platinum, (ii)*, both electrolytic cell and reference electrode were in a thermostat. As there was no liquid potential between them in both cases, the equilibrium potential of oxygen electrode against mercuric oxide reference electrode is calculated from the free energy difference of the following reaction,



Owing to Lewis and Randall⁽⁷⁾, and Shibata and Murata⁽⁸⁾, the equilibrium potential of reaction (2) is as follows:

T °C	18	25	35	45	65
E_T° (mv.)	302.7	299.5	293.5	288.0	276.0

The overvoltage is therefore calculated, subtracting E_T° from measured potential difference.

Results. Case A. Pt, after 30 minutes from closing of the circuits. (Method (i))*.

Overvoltage was measured in the range of temperature of 18° to 65°C, and in the range for current density D_A of 10^{-5}

(6) H. Eyring, et al., "The Theory of Rate Processes", 587 (1941).

(7) Lewis and Randall, "Thermodynamics", 484 (1923).

(8) E. Shibata and F. Murata, *J. Chem. Soc. Japan*, **52** (1931), 393.

* Refer to "Summary".

to 10^{-2} A./cm.² To obtain reproducible results, electrode had been cathodically polarized previously for 2 to 3 minutes at a current density which was the same as that of anodic polarization of former run. The length of time of the cathodic polarization was almost uneffective.

The relation of the increase of potential with time to D_A was contrary to the Hickling and Hill's observation,⁽⁹⁾ that is, the potential increase per unit time was the greater in the present case, the higher was the D_A . The mean potential increase per 10 minutes (between 20 minutes to 30 minutes from closing of circuit) were zero and 65 mv. for D_A 's of 10^{-5} and 10^{-2} A./cm.², respectively. Two to ten runs, according to the reproducibility, were carried out in the same condition. Mean values of overvoltage ($\bar{x}$), and their unbiased estimates of variance ($\hat{\sigma}_{\bar{x}}^2$) of $\bar{x}$ are compiled in Table 1.

Table 1.

Temp. (°C)	A./cm. ²	10^{-5}	10^{-4}	10^{-3}	10^{-2}
18	$\bar{x}$ (mv.)	491	668	816	1253*
	u.e.v. (mv. ²)	446	57	100	157
35	$\bar{x}$	430	620	764	968
	u.e.v.	42	51	36	154
45	$\bar{x}$	361	552	737	904
	u.e.v.	189	194	232	58
65	$\bar{x}$	303	435	670	825
	u.e.v.	836	100	62	0

u.e.v. = Unbiased estimate of variance.

Except the figure with asterisk, they hold the linearity in overvoltage vs. $\log D_A$ curves, Fig. 1. Making u. e. v. as weight, the coefficient of the Tafel's equation,

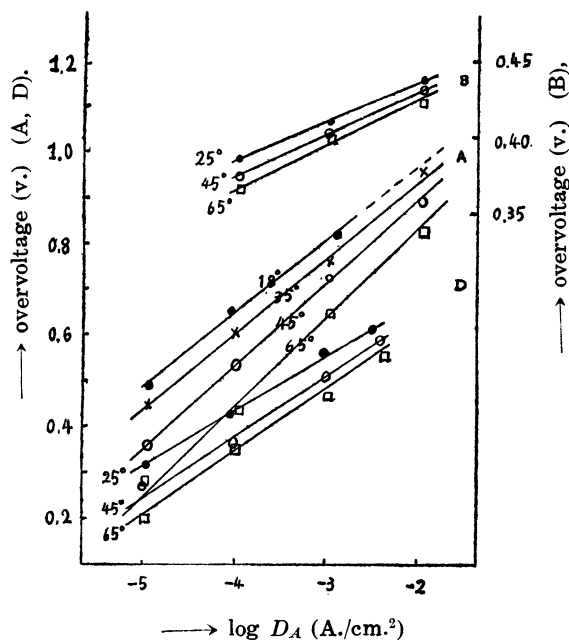
$$\text{overvoltage (mv.)} = a + b \log_{10} D_A \text{ (A./cm.²)},$$

is calculated for each case of the above measurements through the method of least square, as Table 2, where the error represents the mean square deviation.

Table 2.

Temp. (°C)	a	b	α
18	1308±50	162.5±14.1	0.356±0.031
35	1232±14	172.2± 3.7	0.355±0.008
45	1271±22	179.4± 2.1	0.352±0.004
65	1223±18	192.1± 5.7	0.349±0.010
mean.....0.353±0.017			

(9) A. Hickling and S. Hill, *Discussions Faraday Soc.*, No. 1 (1947), 237.

Fig. 1. Overvoltage vs. $\log D_A$.

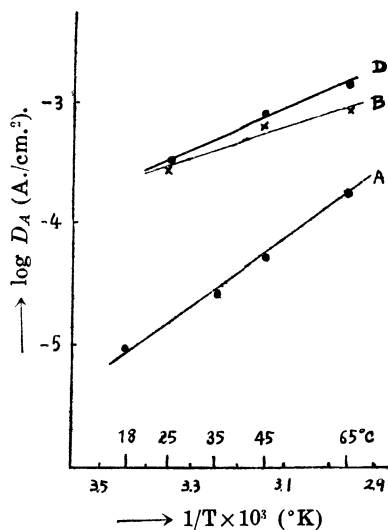
A: Pt, 30 minutes after closing of the circuit.

B: Magnetite, at the stationary state.

D: Pt, by oscillographic method.

From Fig. 1 and Table 2, we have the following relation at overvoltage of 500 mv., as in Fig. 2,

$$\log D_A = 3.88 - (2.58 \pm 0.41) \times 10^3/T. \quad \dots\dots\dots (3)$$

Fig. 2. $\log D_A$ vs. $1/T$.

From Eq. (1), and taking errors into consideration, activation energy has been found to be 15.9 ± 2.0 kcals. This value is independent of overvoltage.

Case B. Magnetite, at stationary state. (Method (iii)). Temperature range was from 25 to 65°C, and range for D_A was from 10^{-4} to 10^{-2} A./cm.² Stationary potential was obtained after several minutes from closing of circuit and no previous cathodic polarization was carried out. At D_A smaller than 10^{-5} A./cm.², overvoltage was much lower than that expected. Mean values of two to four runs were plotted in Fig. 1. The unbiased estimate of variance, zero to 42 mv.², was much smaller in this case than in Case A, and through the above mentioned procedures, coefficients were calculated as in Table 3.

Table 3.

Temp. (°C)	a	b	α
25	492.5 ± 6.3	26.0 ± 2.5	2.26 ± 0.22
45	491.4 ± 3.1	28.6 ± 1.3	2.21 ± 0.17
65	491.3 ± 10.0	29.8 ± 4.0	2.25 ± 0.30
mean..... 2.24 ± 0.23			

Therefrom we have the following relation at overvoltage of 400 mv., as in Fig. 2,

$$\log D_A = 0.524 - (1.207 \pm 0.086) \times 10^3/T. \quad \dots\dots\dots (4)$$

Thus, activation energy on magnetite was calculated from Eq. (1) as 26.2 ± 3.2 kcals.

Case C. Natural graphite, at stationary state. (Method (iii)). Experiments on graphite were carried out in almost the same method as on magnetite, but the range in which the linear relation of Tafel's equation held was so narrow that the activation energy could not be calculated.

Case D. Pt, by oscillographic method. (Method (ii)). Temperature range was from 25° to 65°C, and range for D_A was from about 10^{-5} to 4.6×10^{-3} A./cm.² As for current density of previous cathodic polarization, one tenth of D_A was most preferable, and variation of its duration, 1 to 3 minutes, were not effective on the potential. After the cathodic polarization, the current was reversed, and the built-up curves of anodic potential were recorded. That point which had the maximum curvature on this curve was determined by eye-measurement. Assuming that the adsorption monolayer of oxygen atoms had been completed at this point, overvoltage was calculated subtracting the equilibrium potential, Eq. (2), from the potential of this point. Period of rotation of drum, which was 2 to 6 minutes in these case, was not effective in

determining this point. Mean values of about six runs are plotted in Fig. 1. The unbiased estimates of variance are smaller than 50 mv.², except a very few anomalous points. Coefficient of Tafel's equation was calculated as in Table 4.

Table 4.

Temp. (°C)	a	b	α
25	925.6 ± 9.3	120.5 ± 2.8	0.492 ± 0.007
45	902.0 ± 15.3	131.9 ± 4.6	0.479 ± 0.007
65	804.7 ± 9.2	136.3 ± 2.6	0.492 ± 0.009
			0.448 ± 0.008

From Table 4, we have the following relation at overvoltage of 500 mv., as in Fig. 2,

$$\log D_A = 1.76 - (1.57 \pm 0.11) \times 10^3/T. \dots\dots\dots (5)$$

Activation energy is therefore, 13.8 ± 0.6 kcals.

Discussions. Values of activation energy of anodic oxygen-producing reaction reported hitherto and those determined newly by the present author are summarized in Table 5. As only E_{11} was to be calculated from the Bowden's experiments, true activation energy defined in Eq. (1)

Table 5.

Researcher	Electrode	Electrolyte	Method	Calculation	$\Delta H^\ddagger$ (kcal.)	α	Temp. (°C)
Bowden (1)	Pt	N/5 H ₂ SO ₄	Oscillograph	I*	14.3* 13~14**	0.5	0-81
Yoneda	Pt	N/10 NaOH	"	I	13.8 ± 0.6	0.49	25-65
	"	"	(i)	"	15.9 ± 2.0	0.39	18-65
	Magnetite	"	(iii)	"	26.2 ± 3.2	2.24	25-65
Stout (2)	Pt	"	?	?	25.3	1.0	18-31
Audubert (3)	Pt	N NaOH	?	?	8.3	0.12	?
	"	0.001 N NaOH	?	?	3.1	0.12	?

* Corrected by the present author.

** Estimated value after taking the liquid potential in consideration.

was re-calculated. After estimating the temperature coefficient of standard single electrode potential of oxygen, $dE_r^0(\text{O}_2)/dT$, to be -1 mv./°C, from entropies of hydroxyl ion and so on, and as for that of dissociation constant of water, neglecting the liquid potential between both cells at different temperatures, more correct value of 14.3 kcals. was obtained. Taking the fact into consideration that in acid solution potential of the higher temperature side of liquid contact is less noble than of lower side, more correct value, 13-14 kcals., was obtained.

The Stout's value is too large. The source of this error seems to be that the temperature range in which his experiments were performed was too narrow, and moreover he neglected the influence of time on determining the potential, and it might make α too large, as was pointed out by Bockris.⁽¹⁰⁾

On the contrary, the Audubert's value of α is too small, and his small value of the activation energy may be led herefrom.

The activation energy on platinum measured by the ordinary method and by oscillographic method agreed with each other. This fact means that there is scarcely any difference between the reaction on so-called monolayer of oxygen atom and that on oxide film which is assumed to be deposited on platinum surface after a certain period of anodic polarization. On the other hand, the discrepancy of value of activation energies and α 's between of platinum and of magnetite suggests a discontinuous property between metal and oxide anodes.

Now let us compare the results of the present author in alkaline solution to that of Bowden in acid solution. Method for measurement and calculation are common in both cases. Activation energies and α 's are almost the same. Absolute value of overvoltage measured by Bowden, however, is about 250 mv. higher than that by the author, though, according to the former experiment of the author,⁽¹¹⁾ the overvoltage in aqueous solution of N/10 H₂SO₄ measured by the same method as in Case A was, on the contrary, 100 mv. lower than in alkaline solution. Hoar⁽¹²⁾ made an experiment in acid solution by a similar method to Case A, and his values of 10^{-5} and 10^{-4} A./cm.² are almost the same as the one in alkaline solution above mentioned.

Putting these facts together, the present author suggests the following hypothesis:

In ordinary solution, either acid or alkaline, oxygen is evolved on platinum anode through the same rate-determining step from the same reactant.

Summary.

Activation energies of anodic oxygen-producing reaction on electrode of platinum, magnetite, or natural graphite were measured in aqueous solution of N/10 NaOH under stirring by the stream of oxygen gas, at temperature from about 25° to 65°C. On platinum anode, overvoltage was measured by two methods, (i) by the ordinary method just after 30 minutes from the time of closing the electric circuit, and (ii) by the oscillographic method. The activation energy calculated herefrom was

(10) J. O'M. Bockris, *Discussions Faraday Soc.*, No. 1 (1947), 252.

(11) Y. Yoneda, *J. Chem. Soc. Japan*, in press.

(12) T. P. Hoar, *Proc. Roy. Soc. London*, A **142** (1933), 628.

found 15.9 ± 2.0 kcals. by (i) method, and 13.8 ± 0.6 kcals. by (ii) method. On magnetite and natural graphite, overvoltage was measured by (iii) ordinary method at the stationary state which was obtained after a few minutes. Activation energy of the former was found to be 26.2 ± 3.2 kcals., and that of the latter is not obtained. The activation energy on platinum by oscillographic method is consistent with that measured by F. P. Bowden in the aqueous solution of $N/5$ H_2SO_4 , which is 13–14 kcals. after being corrected about the temperature coefficient of oxygen equilibrium potential. These facts suggest that the anodic oxygen-producing reaction on platinum proceeds through the same rate-determining step both in acid and alkaline solutions, and the mechanism is rather different on platinum from the one on magnetite.

The author wishes to express his grateful thanks to Professor N. Kameyama and Assistant Professor T. Mukaidou for their kind guidance in this work, and for their kindness in reading the original manuscript.

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The Configurations of Δ^5 -Cholestenone Oxides.⁽¹⁾

By Yoshiyuki URUSHIBARA and Misao CHUMAN.

(Received October 28, 1949.)

L. Ruzicka and W. Bosshard⁽²⁾ were unable to prepare an oxide of Δ^5 -cholestenone by oxidation of α -cholesterol oxide with chromic acid, but obtained two stereoisomeric oxides from the action of perbenzoic acid on Δ^5 -cholestenone (I). In analogy with cholesterol oxides, they called the compound with higher melting point (m. p. 202°) " α -oxide" and the isomeride with lower melting point (m. p. 122°) " β -oxide". The 5,6-position of the oxido group was demonstrated by transforming the " β -oxide" into the known cholestanedione-(3,6). For the " α -oxide" such an evidence was lacking but the 4,5-position of the oxido group which might result from displacement of the double bond was considered improbable from the fact that Δ^4 -cholestenone did not give an oxide with perbenzoic acid.

(1) Abstract from the doctor theses by M. Chuman. Read before the monthly meeting of the Chemical Society of Japan on March 8, 1947.

(2) *Helv. Chim. Acta*, **20** (1937), 244.

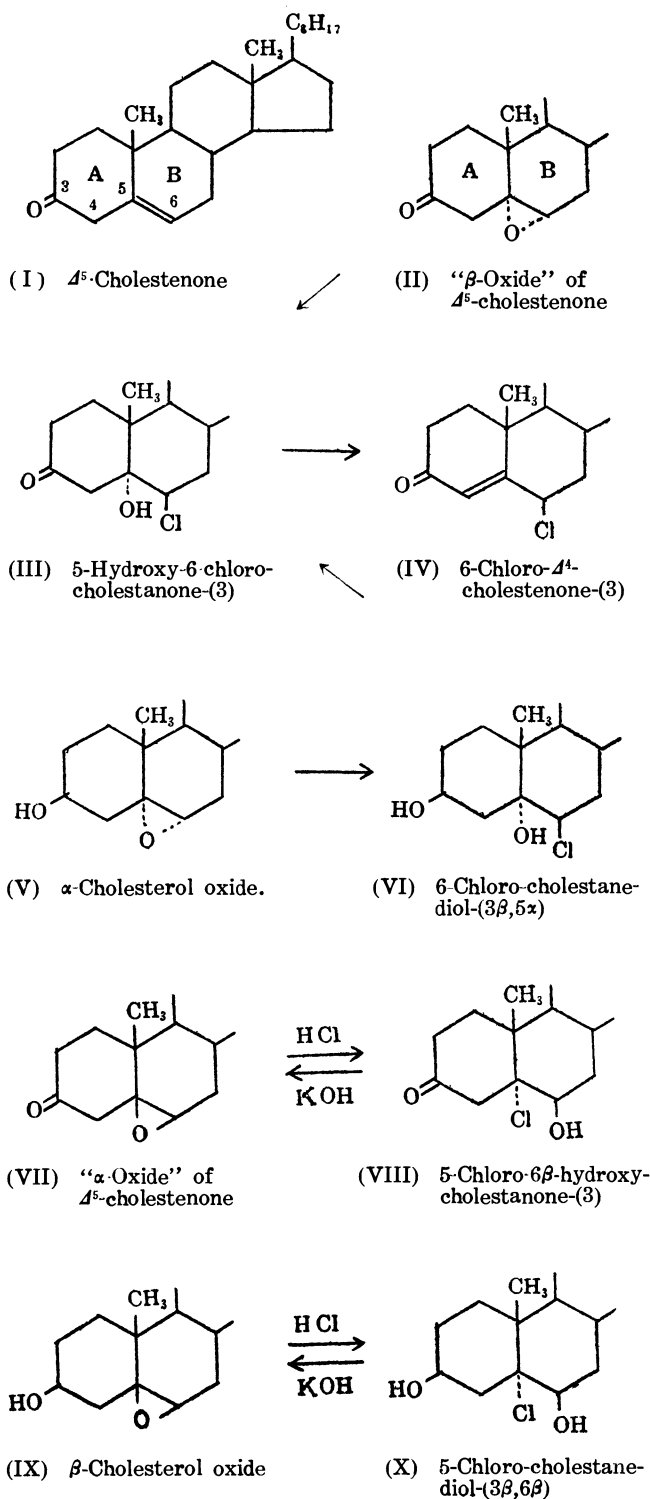
The configurations of cholesterol oxides had already been deduced by one of the present authors,⁽³⁾ while those of Δ^5 -cholestenone oxides remained undetermined. The authors attempted to correlate Δ^5 -cholestenone oxides with cholesterol oxides, but, in spite of every effort, the aimed transformation of the former into the latter, or *vice versa*, was not attained. The undesired changes experienced during the unsuccessful attempts will not be recorded in this paper.

In the previous paper⁽⁴⁾ one of the authors presented a stereochemical representation of the structures of cholesterol oxides and the courses of the scission reactions of the oxido ring in them. As the structures of Δ^5 -cholestenone oxides can be represented quite similarly, it may reasonably be assumed that the rules for the oxido ring rupture of cholesterol oxides hold good as well in the case of Δ^5 -cholestenone oxides. Namely, the α -oxido ring is opened between carbon atom 6 and the oxido oxygen atom, while the β -oxido ring between carbon atom 5 and the oxido oxygen atom; the oxygen atom with the hydrogen atom derived from the addenda forms a hydroxyl group with the original configuration; and the residues from the addenda enter the carbon atom cut off from the oxido oxygen atom, all attached to carbon atom 5 taking the α -configuration, thus the β -oxido ring as well as the α -oxido ring producing cholestane derivatives on scission, and certain groups including the hydroxyl group from water and the acetoxy group from acetic acid being determined to assume the β -configuration at carbon atom 6. Now, hydrogen chloride has afforded the key to the determination of the configurations of Δ^5 -cholestenone oxides. The configurations of the scission products described below have been inferred from the above-mentioned rules, and the accompanying formulas assume that the chlorine atom entering carbon atom 6 takes the β -configuration like the hydroxyl and the acetoxy groups.

The " β -oxide" of Δ^5 -cholestenone gave a scission reaction analogous to that of α -cholesterol oxide: The action of hydrogen chloride on α -cholesterol oxide (V) gave 6-chloro-cholestanediol-(3 β ,5 α) (VI), m.p. 168–169°, which was then oxidized to 5-hydroxy-6-chloro-cholestanone-(3) (III), m. p. 200°, and dehydration of the latter with hydrogen chloride yielded 6-chloro- Δ^4 -cholestenone-(3) (IV), m. p. 125–126°. The same 6-chloro- Δ^4 -cholestenone-(3) was obtained by the action of hydrogen chloride on the " β -oxide" of Δ^5 -cholestenone. In the latter case the intermediate 5-hydroxy-6-chloro-cholestanone-(3) lost water at once in conformity with its structure of a 3-ketone with a tertiary hydroxyl group at carbon atom 5.

(3) Y. Urushibara, This Bulletin, **16** (1941), 182.

(4) Y. Urushibara, This Bulletin, **22** (1949), 132.



The " α -oxide" of Δ^5 -cholestenone behaves like β -cholesterol oxide: The former gave a product on the action of hydrogen chloride. It differed from 5-hydroxy-6-chloro-cholestanone-(3) (III), m. p. 200° , and melted at 125 – 126° , but a deep depression of the melting point was observed in admixture with 6-chloro- Δ^4 -cholestenone-(3) (IV) with the same melting point. Treatment with alcoholic potash or with many other reagents not enumerated here regenerated the " α -oxide" of Δ^5 -cholestenone, while neither 5-hydroxy-6-chloro-cholestanone-(3) (III) nor 6-chloro- Δ^4 -cholestenone-(3) (IV) gave either oxide of Δ^5 -cholestenone on the action of alcoholic potash or on any other treatment. Hence, the product from the action of hydrogen chloride on the " α -oxide" of Δ^5 -cholestenone is 5-chloro-6 β -hydroxy-cholestanone-(3) (VIII), and its formation from the " α -oxide" by the action of hydrogen chloride and the regeneration of the oxide from it by the action of alcoholic potash correspond to the behaviour of β -cholesterol oxide (IX) which gives 5-chloro-cholestanediol-(3 β ,6 β) (X) with hydrogen chloride and is regenerated from the latter by the action of alcoholic potash.

The observations outlined in the preceding paragraphs lead to an assignment of a β -oxido (VII) and an α -oxido (II) structures, respectively, to the " α -oxide" and the " β -oxide" of Δ^5 -cholestenone. As both cholesterol oxides are derivatives of cholestanol,⁽⁴⁾ both Δ^5 -cholestenone oxides are derivatives of cholestanone, and consequently the names expressing the stereochemical structures should be 5,6 β -epoxy-cholestanone-(3) for the " α -oxide" and 5,6 α -epoxy-cholestanone-(3) for the " β -oxide".

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